ISSN 0255-7193

CLAY RESEARCH

Vol. 31, No. 2

December, 2012

IOS Press

Overseas distribution
IOS Press, The Netherlands

THE CLAY MINERALS SOCIETY OF INDIA
Division of Soil Science and
Agricultural Chemistry
Indian Agricultural Research Institute
New Delhi-110 012, India

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Print + online access	Rs. 1,800.00	$ 350.00
Online access	Rs. 600.00	$ 150.00
Print	Rs. 1,200.00	$ 200.00

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Clay Research, Vol. 31, No. 2, pp. 70-78 (2012)

Retention of Boron – A Plant Micronutrient Using Pure Clay

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Abstract: *Boron is an essential micronutrient with narrow range of deficiency and toxicity. To predict B behavior in soils and its influence on plants, it is crucial to understand the mechanisms of B sorption by mineral phase. The adsorption of B increased as the pH increased up to 10, thereafter it decreased with further increase in the pH. The amount of boron adsorbed increased slightly at 4 hours of time and decreased as the time was increased to 6 hours thereafter an increase and decrease was observed for subsequent variation in contact time. As the concentration of B increased in the solution the adsorption of B increased. Yet the percentage of B adsorbed decreased. The importance to study the effect of varying concentration was to highlight the availability of this trace element, which enters the soil by number of path ways. At moderate levels of concentration the soil will act as repository for this trace element, but at higher concentration it may be transported to ground water table. The amount of B adsorption was more in presence of* Ca^{+2} *ions. The B adsorption may be more in alkaline soils with high clay content and high* $CaCO_3$ *content. The adsorption of B was initially rapid followed by a slow process. As the amount of clay increased, for a given initial concentration, the amount of adsorption increased. Application of Freundlich isotherm and Langmuir isotherm to the adsorption of boron were satisfactory. The applicability of the Lagergren model to adsorption of boron was not satisfactory.A plot of Ln Ci/Ce Vs t indicated that the adsorption of B does not follow the first order kinetics. The value of* R_L*, a dimensionless equilibrium parameter, was 0.05363 indicating favorable adsorption.*

Key words : Boron, Micronutrient, Adsorption, Montmorillonite

Boron is an essential element for plant growth. It is important in plant metabolism since it is involved in cell structure and sugar translocation. Boron enters into the environment mainly through the weathering of rocks, boric acid volatilization from sea water, and volcanic activity (UNEP, EHC-204). B is also released from anthropogenic sources, but to a lesser extent.

There has been broad interest in studying the interaction between B and soil constituents because of the relatively small range between B concentrations that cause

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deficiency and toxicity symptoms in plants. Abundant literature exists on B sorption by soil and soil minerals, yet the mechanisms of B sorption are not yet fully understood. Insight into mechanism controlling B partitioning between solid and solution phases is crucial for a qualitative understanding of behavior of B in soil and its effect on plants (Chumming and Suarez, 1997). Several factors are known to influence B adsorption reaction, including pH, initial B concentration in solution, ionic strength, temperature, and presence of other metals and ligands and the types of clay mineral surfaces. (Mattigod *et al.*, 1985)

The present study emphasizes upon the importance of ion pair formation on B adsorption in Ca^{+2} dominated electrolytic solution (Mattigod *et al.*, 1985). The object of this study is to obtain reliable data on adsorption of B by montmorillonite clay surface under clearly defined conditions of pH, B concentration, adsorbent dosage, time and in presence of a competing ion. Although the adsorption of B has been shown to differ with the form of the exchangeable cation, this effect has been attributed by some to the influence of the exchangeable cation on the thickness of the diffuse double layer and the accessibility of B to potential adsorption sites (Keren and Gast, 1981). This type of data will be helpful in understanding adsorption-desorption of B in soil and subsequent transport to the groundwater.

Materials and Methods

To investigate the adsorption kinetics of B using montmorillonite clay, a stock solution of 10 mg B/L was prepared by dissolving 0.0572 g of H_3BO_3 acid in 1000 ml of water. All reagents used were of analytical grade and B-free distilled water was used for the preparation of the reagents. The work was carried out using polyethylene containers, Pyrex glassware and china dishes.

Montmorillonite clay used for the study was purchased and it was characterized using ARL (Switzerland) X-Ray Fluorescent Spectrum 9800Xp., To study the effect of pH on the adsorption of B by the mineral clay, 100 ml of the stock solution was taken in each of the six polyethylene beakers. The pH was adjusted to 2, 4, 6, 8, 10 12 using diluted H_2SO_4 and ammonia solution. To each beaker 5 g of montmorillonite clay was added and the concentration of the B remaining after 60 minutes of contact time was estimated using a standard method (Bassette *et al.*, 1978). Similarly to study the effect of contact time, the time was varied over 60, 120, 180, 240, 300, 360, 420 minutes, and also 24 and 48 hours, at the optimum pH, and then subsequently the adsorbent dosage was varied as 2, 4, 6, 8 and 10 g. After setting the optimum conditions the initial concentration of the boric acid solution was varied between 1 and 10 mg/L.

To study the effect of Ca^{2+} ion on the adsorption of B, a binary solution was prepared by dissolving required amount of boric acid and calcium carbonate and mixing 50 ml each at equimolar concentration (10 mg/L of B and 10 mg/L of Ca^{2+}) and at higher molar concentration of Ca^{2+} ion than B (10 mg/L of B and 25 mg/L of Ca^{2+}).

The amount of B remaining in the solution was estimated spectroscopically, using Curcumin-oxalic acid reagent by the standard method at 540 nm (Bassette *et al.* 1978)

Results and Discussion

Adsorption reactions occurring at the solid-liquid interface area are significant mechanism controlling trace element activities. The adsorption of B (III) using montmorillonite clay was investigated in a batch study. The results of the studies on adsorption of B by using the above adsorbent in a batch experiments work are presented below.

The adsorption of B was investigated as a function of pH. Boron adsorption increases with increasing pH and diminishes abruptly at higher pH. The amount adsorbed increases till pH 4 then there is a slight decrease and it increases till the pH reaches 10. At pH 10 the percentage of B adsorbed is 40%. (Fig.1).

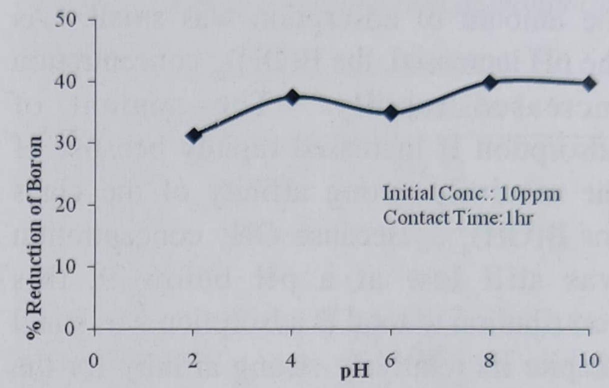

Fig. 1. *Effect of pH on the adsorption of Boron (III) using Montmorillonite clay.*

At lower pH the H^+ ions compete with BO_3^{3-} for adsorption site. B adsorption increases with increasing pH until a peak of adsorption is reached. The increase in B adsorption is attributable to the ionization of boric acid. Above this peak, B adsorption decreases as pH continues to increase. B adsorption at high pH depressed both because of increasing competition from hydroxyl ions and increasing negative charge on the clay edge. The influence of the negative permanent change on B adsorption on the particle edge is significant for montmorillonite (Keren and Mezuman, 1981). The maximum development of adsorption site occurs at pH equivalent to the pKa of boric acid approximately at pH 9.1 as has been reported in the literature (Mattigod *et al.*, 1985). The B toxicity has been reported to have increase in alkaline soils.

The response of the systems to variations in pH can be explained as follows: Below pH 7, $B(OH)_3$ predominated, but because the affinity of the clay for this species was relatively low, the amount of adsorption was small. As the pH increased, the $B(OH)_4^-$ concentration increased rapidly. The amount of adsorption B increased rapidly because of the relatively strong affinity of the clays for $B(OH)_4^-$. Because OH^- concentration was still low at a pH below 9, this contribution to total B adsorption was small despite its relatively strong affinity for the clays. Further increase in pH resulted in an enhanced OH^- concentration relative to $B(OH)_4^-$, and B adsorption decreased rapidly due to the competition of OH^- for the adsorption sites.(Keren and Mezumen, 1981)

The B adsorption was characterized by an initial fast reaction followed by a slow process. Slow rate of reaction could be attributed to diffusion of B to the adsorbent site (Krishna Swamy *et al.*, 1997). To study the effect of contact time on B adsorption, the contact time was varied between 60 minutes to 48 hours, at optimum pH of 10. The amount of adsorption did not vary much with increasing the time of contact from 60 to 180 minutes. The amount adsorbed increased slightly at 4 hours of time and decreased as the time was increased to 6 hours thereafter an increase and decrease was observed for subsequent variation in contact time. The solution was equilibrated for 48 hours and the amount of the adsorption was same as that observed at 60 minutes. (Fig. 2).

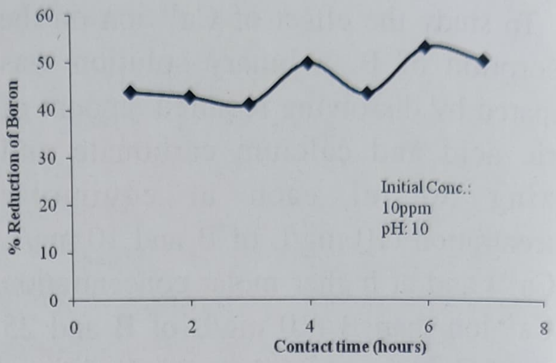

Fig. 2. *Effect of contact time on the adsorption of Boron (III) using Montmorillonite clay.*

This type adsorption – desorption reaction plays an important role in the B deficiency and toxicity to the plants and transport of the B to the ground water. Among all the soil chemical properties, the adsorption - desorption reactions govern the concentration of trace elements in soil solution. Desorption is the key factor controlling the availability and mobility of metal ions in soil (Jeevan Rao, 1999)

Though every solid is a potential adsorbent, the physico - chemical nature of the adsorbent have profound effects on both rate and capacity of adsorption. It has been reported in literature that B adsorption reactions on clay minerals is ligand exchange with reactive surface hydroxyl groups on the broken edges. In the present study the percentage of B adsorption at a dosage of 2g/100ml was 58.75% whereas at a dosage of 8g/100ml , 71.2% adsorption took place (Fig. 3).

The effect of initial concentration of solution on B adsorption indicated that the B adsorption decreased with an increase in initial concentration. The concentration

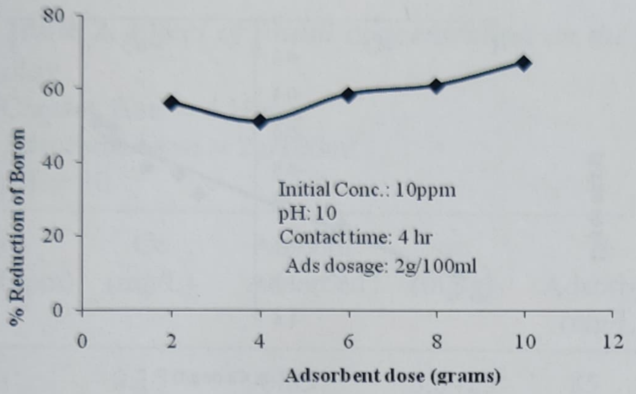

Fig. 3. *Effect of adsorbent dosage on the adsorption of Boron (III) using Montmorillonite clay.*

Table 1. *Chemical composition of montmorillonite clay*

Composition	Percentage
Cao	94.71
Fe_2O_3	4.15
K_2O	0.7
Al_2O_3	0.16
TiO_2	0.12
MgO	0.12
SiO_2	0.32

of the solution varied between 1 to 10 mg/L, which is the upper limit of B concentration in the Earth's crust (David Lide, 1997). As the concentration of B increased in the solution, the adsorption of B increased. Yet the percentage of B adsorbed decreased (Arora and Chahal, 2002). This may be because of an increase in the ratio of adsorbate to adsorbent. (Fig. 4 and Table 1). The importance to study the effect of varying concentration was to highlight the availability of this trace element, which enters in the soil by number of path ways. At moderate levels of concentration the soil will act as repository for this trace element, but at higher concentration it may be transported to ground water table.

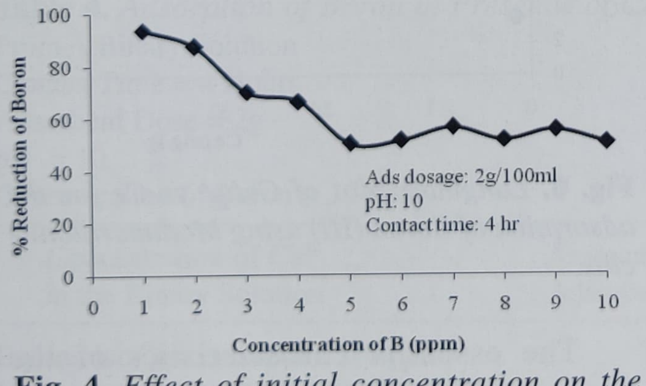

Fig. 4. *Effect of initial concentration on the adsorption of Boron (III) using Montmorillonite clay.*

Reardon (1976) established that borate ions form soluble complexes with alkali and alkaline earth cations. Thus, the formation of borate complexes in solution may affect the adsorption of this element on mineral surface. According to Baes and Mesmer (1976), B in solution can exist as boric acid molecule ($H_3BO_3^0$), borate ion ($B(OH)-_4^{-1}$), and as various polymeric species. The distribution of various species at ambient temperature and pressure is a function of pH and total B concentration. Borate ions can also exist in soluble complex forms with alkali, alkaline earth, and various trace metal cations. The effect of presence of Ca^{2+} ions on the adsorption of B has also been investigated at lower concentration and at higher molar concentration of Ca^{2+}. The adsorption increased with increasing concentration of Ca^{2+} ions. The percentage adsorption at equimolar concentration of B and Ca^{2+} was 75% and the percentage adsorption at higher molar concentration of Ca^{2+} was 83.75%. In either case the percentage adsorption is more than when B alone was present in the solution. (Table 3) At pH 9.5 and above the main absorbing species is $B(OH)_4$ where in presence of alkali earth metal ion Ca^{2+} the absorbing species may be $B(OH)_4^-$ Ca $B(OH)_4^+$ (Mattigod *et al.*, 1985). It is a well established fact that at higher pH the negative charge on clay surface are dominant. The edge sites on clays have greater affinity for monovalent ion pairs than for divalent free metal cations because the magnitude of free energy of desolvation is much less for monovalent ion pair as compared to divalent free cations (Stumm and Belinski 1973, Sposite *et al.*, 1981, Sposite *et al.*, 1983). Therefore, Ca $B(OH)_4^+$ species might have occupied the cation exchange site on montmorillonite clay in addition to $B(OH)_4^-$ ions occupying anion exchange sites. Thus the difference in the B adsorption could be attributed to the difference in the concentration of adsorbable B species in $CaCl_2$ medium.

Freundlich isotherm was plotted between Log Ce and Log Qe and was linear (Fig. 5) and the equation for Freundlich isotherm is y = 0.514x +0.0505.

The Langmuir isotherm plotted between Ce and Ce/qe was linear over a wide range.

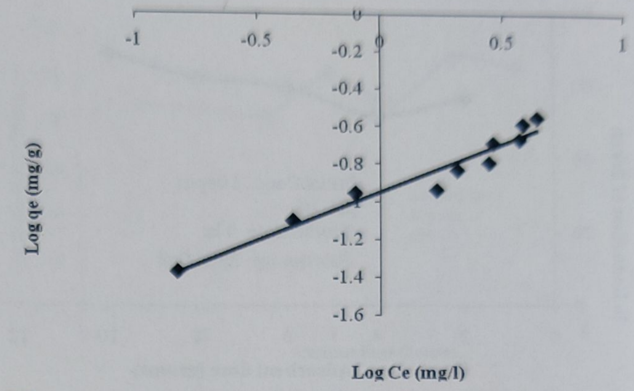

Fig. 5. *Freundlich plot of log Ce vs Vs log qe for the adsorption of Boron (III) using Montmorillonite clay.*

The values of the Langmuir constants Co and b are given in the table 2, which were calculated from slopes and intercepts of the Langmuir plot (Fig. 6). The correlation factor was 0.86 and the equation for Langmuir isotherm is y = 0.29142x+5.7522

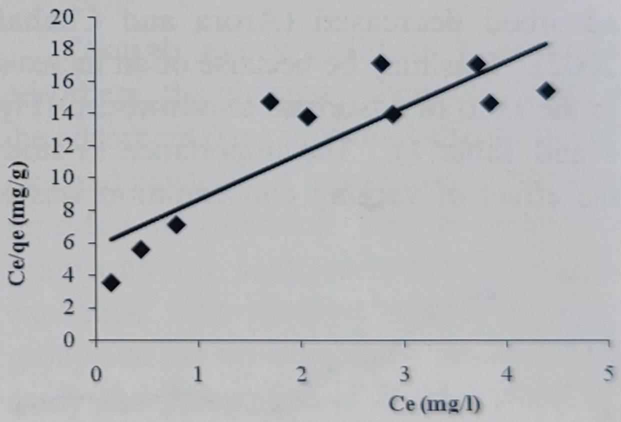

Fig. 6. *Langmuir plot of Ce/qe vs Ce for the adsorption of Boron (III) using Montmorillonite clay.*

The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless equilibrium

Table 2. *Effect of initial concentration on the adsorption of Boron (III) using Montmorillonite clay*

Contact Time = 4 Hours
Adsorbent Dose = 2g/100ml
pH = 10

Ci (ppm)	Ce (mg/L)	Amount Adsorbed	qe (mg/g)	% Adsorbed (mg/L)	Log Ce	Log qe	K X 10^{-3} (min^{-1})	DG ($J.K^{-1}mol^{-1}$)
1	0.15	0.85	0.0425	85	-0.8239	-0.13716	7.9046	-4632.76
2	0.44	1.575	0.0787	78.75	-0.3565	-0.110374	6.3088	-3697.49
3	0.7875	2.2125	0.1106	73.75	-0.1037	-0.0956146	3.5821	-3266.18
4	1.7	2.3	0.1150	57.5	0.2304	-0.939302	3.5652	-2089.53
5	2.0625	2.9375	0.1468	58.75	0.3143	-0.833052	3.6896	-2162.43
6	2.775	3.225	0.1612	53.75	0.4432	-0.79250	3.2129	-1883.04
7	2.8875	4.1125	0.2056	58.75	0.4605	-0.686924	3.6896	-2162.43
8	3.7	4.3	0.2150	53.75	0.5682	-0.667561	3.2129	-1883.04
9	3.825	5.175	0.2587	57.5	0.5826	-0.58711	3.5652	-2089.53
10	4.375	5.625	0.2812	56.25	0.6409	-0.550907	3.444	-2018.74

Table 3. *Adsorption isotherm constants for adsorption of boron using Montmorillonite clay*

Freundlich Isotherm constant				Langmuir Isotherm constant			
K (mg/g)	1/n	R2 correlation	Coefficient (mg/g)	Qo (mg/L)	b	R2	Coefficient correlation
0.11233	0.5140	0.9458	0.97253	3.431	1.676	0.7513	0.8667

Table 4. *Adsorption of Boron in Presence of Ca^{2+} Ions*

From A Binary Solution
Contact Time = 4 Hours
Adsorbent Dose = 2g
pH = 10
Concentration of Boron = 10 ppm

Concentration of Ca^{2+} in the Binary Solution	Amount of Boron Adsorbed (Mg/L)	Amount of Boron Remaining (Mg/L)	Percentage Adsorbed
Equimolar Concentration (10 ppm)	7.5	2.5	75%
Higher molar Concentration (25 ppm)	8.375	1.625	83.75%

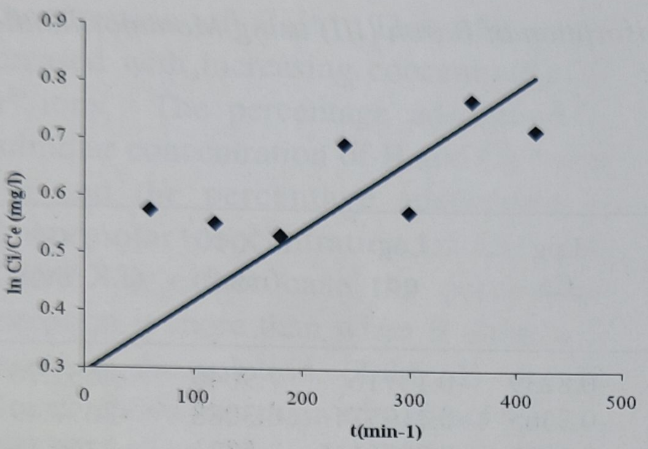

Fig. 7. *Plot of In Ci/Ce vs t for the adsorption of Boron (III) using Montmorillonite clay.*

parameter R_L. The value of R_L was 0.05363 indicating favourable adsorption.

The results were analyzed in the light of the Lagergren model. A non linear relationship was observed among the plotted parameters indicating that the applicability of the above equation to the uptake of the adsorbate is not satisfactory. (Fig. 8)

The molar free energy changes were calculated for varying concentration at 27 °C and the free energy values were obtained (Table 1). The decrease in DG provides a measure of decrease in the concentration of adsorbate in the solute phase. The negative value indicates the spontaneity of adsorption.

A plot of ln Ci / Ce Vs t (Fig.7) showed a non linear graph, indicating that adsorption of B does not follows first order kinetics. The correlation factor is 0.7588.

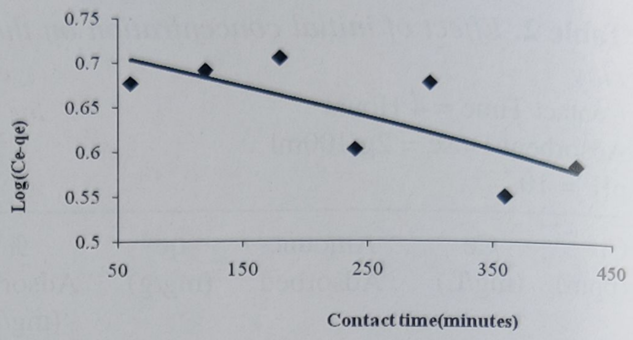

Fig. 8. *Lagergran plot of Log (Ce-qe) vs t for the adsorption of Boron (III) using Montmorillonite clay.*

Acknowledgement

The authors are grateful to the management of the Gitam University, Visakhapatnam for providing the necessary facilities to carry out this work.

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(Received September, 2011; Accepted December 2012)

Clay Research, Vol. 31, No. 2, pp. 79-83 (2012)

Characterization of Miocene Marl of Fez Regions of Morocco after doping with MnO_2

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Abstract: *The Miocene marls or calcareous clay of the southern Rif groove is one of the geological wealth of the two regions of Fez in Morocco. For greater industrial development in Fez regions the present study on calcareous clays was undertaken. Physical and chemical characterization of this clay was carried out before and after doping with MnO_2 following various analytical techniques such as X-ray diffraction (XRD), scanning (SEM) and transmission electron microscope (TEM). The doping of the clays was done at different percentages (5%, 10% and 15%) of MnO_2. The results of the mineralogical analysis of clays before and after this doping show that the peaks appear for pyrolusite. Further characterization of the nano clays by TEM before and after doping, indicated the different nano organization of these oxides in the clay matrix.*

Key word : Marl, Calcareous clays, Manganese oxides, nano-organization.

The use of clay resources by human, mainly in the manufacture of building materials, dates from antiquity. Clay is a cheap and abundant material. However its low mechanical strength and color non-uniformity after cooking limits its added value. The use of an organic reinforcement in a mineral matrix is often a solution to improve the mechanical elements implemented. Economic issues related to the rising costs of these methods (long chemical processes), and their complications, therefore, leads to explore other simple and low cost manufacturing methods such as doping with external material. In this work, we evaluate the influence of the doping on Miocene clay of the region of Fez with manganese oxide.

Materials and Methods

The basic raw material is a clay marl Miocene the region of Fez (Fig. 1). This region is known for its expertise in the field of pottery and tiles.

Samples were taken from the quarry

through a simple process which is similar to that used by potters and artisans to manufacture the tiles and bricks.

Preparation of composite clay / manganese oxide

Many methods have been developed for the synthesis of powders which are widely used in research laboratories and industry (El Yakouti, 2006). These methods can be classified into three main categories viz. gas, liquid or the chemical and solid. In the present study, we used the solid method with the Miocene marls (Bouyahyaoui, 1996), at the nanoscale. We used the marl and doped them by manganese at different percentages (5, 10 and 15%).

The method used for mixing oxide manganese and calcareous clay involved three steps: mixing of precursors, reaction in solid, grinding and calcinations at 400ºC.

In order to follow the homogeneity and the degree of MnO_2 incorporation in the clay sheets several analysis/ techniques were used.

Results

The calcareous clay (Mesrar, 2012) sample was reacted with the blend of three acids (HCl-H_2SO_4-HNO_3). The analysis was carried out in the national centre for scientific and technical research (CNRST in Morocco). The elements are measured by ICP-AES (Jobin Yvan ULTIMA2 model).

The sample contains a high amount of SiO_2, Al_2O_3 and CaO (Table 1). The latter is related to the presence of calcite.

However, the Fe_2O_3 is more related to the presence of pyrite observed in SEM. The presence of CaO leads to a high mechanical strength in marl (Quandil, 2007).

The pH of the samples increases gradually as the electrical conductivity decreases (Table 2).

X-ray diffraction (XRD)

The XRD study was carried out in the (CNRST) with the Philips diffractometer XPERT-PRO" PW 3064, with the Ká radiation of copper.

The sample synthesized by different

Table 2. *Results of pH and electrical conductivity.*

Sample	pH	EC ìs cm^{-1}
Z3 Gross	8.18	1439
Z3 à 5%	8.67	1103
Z3 à 10%	8.67	956
Z3 à 15%	8.99	971

Table 1. *Percentage major elements of the crude marl.*

Elements%	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	MnO_2	Fire loss
Z3	44.5	14.8	7.20	6.20	1.91	3.18	0.83	0.207	18.6

percentages (5.10 and 15%) of manganese oxide showed the presence of crystalline phases from the corresponding metal cation exchanged during doping. The peak intensity increases with the content. This shows the presence of pyrolusite and reflections from the marl are detected (Fig. 1). The illite and kaolinite became amorphous and this was concomitant with the destruction of crystal network (Papin, 2002). In effect, manganese (Mn^{4+}) replaces the silica (Hidalgo, 1999) in the tetrahedral sites and thus this substitution destroys the crystal lattice, because the rate of substitution between silica and Mn^{4+} is 18%.

Scanning electronic microscope (SEM)

The SEM observation were made on finely crushed powders. Then they were made as pellets of 13mm diameter using a pressure of 5 tons for 2 min under vacuum. The microscope used for these observations was Hitachi S-2500, it operated with an acceleration voltage of 16 kV.

The SEM observation of the raw sample shows that the microstructure is formed by a relatively homogeneous clay matrix (Fig.2.A) and the grains are of variable sizes and tabular form , the pores observed (spaces between clusters and in contact with clay-grain clays) are elongated,

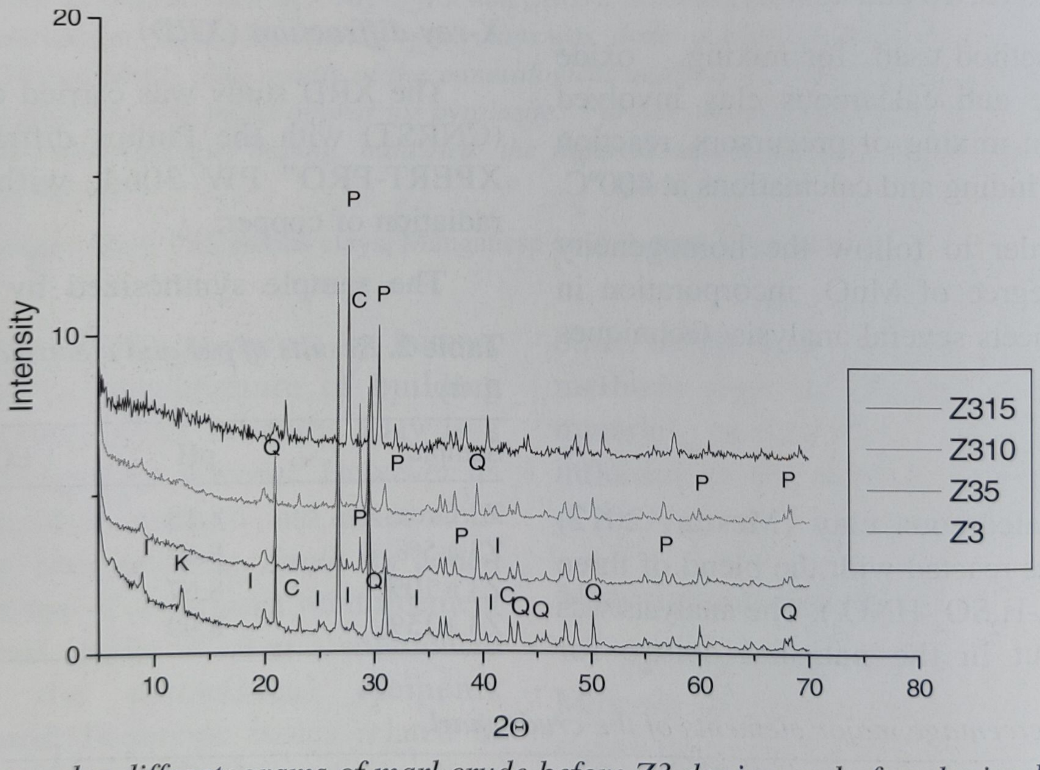

Fig. 1. *X powder diffractograms of marl crude before Z3 doping and after doping by oxide of manganese at different percentages. K = kaolinite, Q = quartz, I = Illite, C = calcite, P = pyrolusite.*

their width was generally less than 5µm (Fig. 2 A). The presence of silica microzone primarily as a structure made of sponge or honeycomb (Fig. 2B), the latter consisted of assembling chips apparently linked by silica. We also note the presence of calcite (Fig. 2C), in significant quantity, which was the result of evaporation of carbonate-rich solution (Papin, 2002). The carbonates consist of an ordered assembly of rods limestone 1 to 2 µm in diameter. They are welded to rhombohedral calcite microcrystals that grow in epitaxial growth on calcareous rods (Fig. 2F). We also noticed slips kaolinites (Fig. 2D).

Transmission electron microscope (TEM)

The powders were finely ground was placed in a sample holder made of copper and carbon. Our samples were observed using a TEM-type FEI TECNAIG12,with an acceleration voltage of 120KV.

The crystals manganese formed are elongated prisms (Fig. 3). It has 3428.88 nm up with length and 531.47 nm in diameter. The crystals are homogeneous and associated with many small crystals.

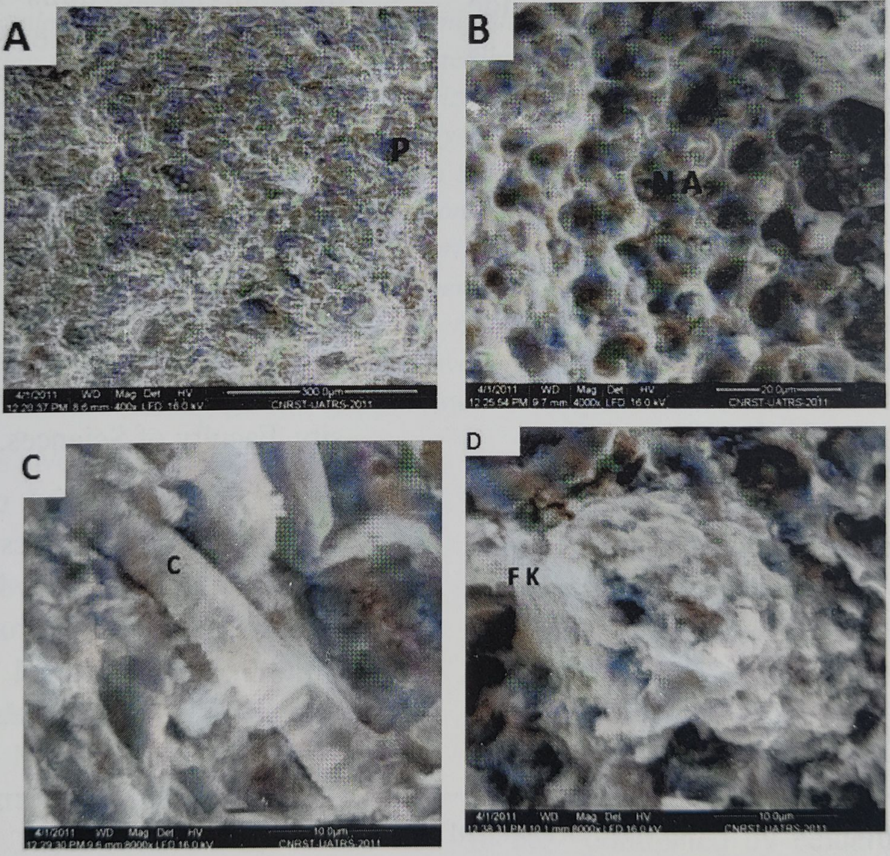

Fig. 2. *The SEM photographs of sample Z3 crude.*

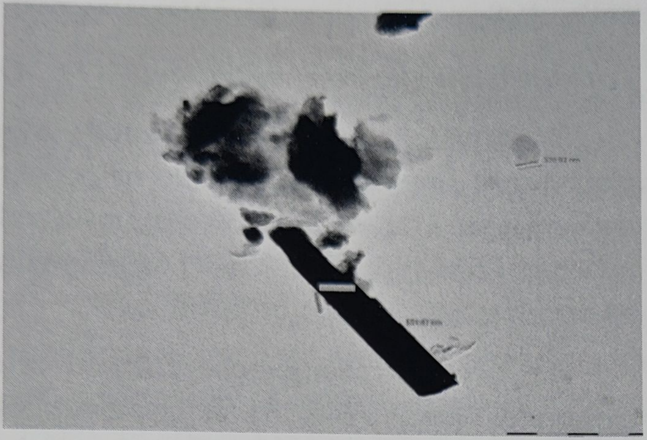

Fig. 3. *The micrograph of sample Z3 after doping marl with oxide manganese at 5%.*

Conclusion

Doping marl with manganese oxide indicated the formation of pyrolusite as Mn^{4+} substituted silica in tetrahedral sites

Acknowledgement

The authors acknowledge the instrumental help rendered by the CNRST, Rabat, Morocco.

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(Received October, 2011; Accepted November, 2011)

Clay Research, Vol. 31, No. 2, pp. 84-93 (2012)

Speciation of Smectites in two Shrink-swell Soils of Central Peninsular India

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Abstract: *Shrink-swell (Vertisols and their intergrades) soils cover an extensive area especially in Peninsular India with smectites as the dominant mineral. It was felt necessary to find out the species of smectites for better management of these soils. Hence, two benchmark Vertisols namely Seloo from Wardha and Saikhindi from Ahmadnagar districts of Maharashtra were chosen for the study. High resolution mineralogical analysis employed through X ray diffraction (XRD) techniques of the silt, total clay and fine clay fractions of both the pedons were carried out along with Greene-Kelly test with only fine clays. Silt (50-2 μm), total clay (<2 μm) and fine clay (<0.2 μm) fractions are dominated by smectite in both the soils; the smectites content increased gradually with decreasing size fraction. The fine clay fractions are mostly composed of smectite with small amounts of vermiculite and traces of chlorite, kaolin and feldspar. Greene-Kelly test indicated that both Seloo and Saikhindi soil fine clays are dominated by beidellite/nontronite over montmorillonite. The Seloo fine clay smectite is composed of 18-26 per cent and 74-82 per cent montmorillonite and beidellite/nontronite, respectively, and for Saikhindi it is composed of 32-41 per cent and 59-68 per cent for montmorillonite and beidellite/nontronite, respectively. However, these fine clay smectites are of low charge dioctahedral nature and therefore may not have any K selectivity. This property appears to have implications in K management of shrink-swell soils of Deccan basalt areas.*

Key words : Vertisols, smectite, speciation, montmorillonite, beidellite/nontronite, K management.

Shrink-swell (Vertisols and their intergrades) soils cover an extensive area especially in the Peninsular India. These soils occupy about 76.4 mha (Bhattacharyya *et al.*, 2009; Mandal *et al.*, 2012) out of which about 30 mha (41%) is in Maharashtra. These soils are developed in alluvium derived from weathering of Deccan Trap basalt. The black soils of the Deccan Trap of India are rich in plagioclase feldspars and yield dioctahedral smectite as the first weathering product (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1993). Earlier these smectites were reported to be dominated by beidellite-nontronite type of minerals (Ghosh and Kapoor, 1982).

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But, the Mg-saturated clays expanded to about 1.8 nm with glycerol vapour. It was thus envisaged by Pal and Deshpande (1987) that the beidellite used for study by Harward *et al*. (1969) had apparently a higher tetrahedral charge. In spite of this fact, knowledge of exact species of smectite group may provide valuable inputs about the genesis of these soils. The information may also be helpful in better management of these soils. Therefore, the present study was undertaken which deals with the nature of speciation in smectites in two shrink-swell soils of the central Peninsular India.

Materials and Methods

Study Area

Two benchmark soils one is Seloo (Typic Haplusterts) from subhumid (dry) part of Wardha district and the other Saikhindi (Vertic Haplustepts), from semi-arid (dry) from Ahmadnagar district of Maharashtra were selected for the present study.

Physical and Chemical Characteristics of the Soils

The physical and the chemical characterization of the soils show higher clay and fine clay in Seloo soils compared to Saikhindi soils (Table 1). COLE and available water content was also higher in Seloo as compared to Saikhindi soils. Organic carbon content was comparable in both the soils. pH, $CaCO_3$ equivalent and ESP were higher in Saikhindi compared to Seloo. There is also slight to moderate problems of sodicity in Saikhindi soils, however, this is largely obliterated by possible presence of zeolites (Pal *et al.*, 2006).

Mineralogical analysis of the Soils

The silt (50-2 μm), total clay (<2 μm) and fine clay (<0.2 μm) fractions of each horizon of two pedons were analysed for qualitative mineralogy by X-ray diffraction (XRD) technique (Jackson, 1979) using a Philips X'Pert Pro diffractometer with Ni-

Table 1. *Some physical and chemical properties of the soils*

Property (units)	Seloo	Saikhindi
Clay (%)	51.5 – 58.2	39.2 – 45.1
Fine clay (%)	43.7 – 52.2	32.1 – 40.1
COLE	0.18 – 0.26	0.18 – 0.22
Available water content (%)	20.2 – 28.9	13.2 – 15.6
Organic carbon (%)	0.32 – 0.97	0.44 – 0.94
pH (1:2, soil: water)	8.0 – 8.4	8.5 – 9.0
$CaCO_3$ equivalent (%)	3.3 – 4.4	14.8 – 23.7
ESP	<1	5 – 8

filtered Cu-Kα radiation at a scanning speed of 2°2θ/min. The semi-quantitative estimates of minerals in the silt, total clay and fine clay fractions were done by the method of Gjems (1967).

Hofmann-KIemen effect (1950) modified by Greene-Kelly (1953) and Lim and Jackson (1986) was performed only on fine clay samples (as total clay contained about 80-90 per cent of fine clays), and the glycerol solvation of the Li-saturated samples were prolonged upto 30-days (Pal and Deshpande, 1987; Kalbande *et al.*, 1992; Bhattacharyya *et al.*, 1993; Ray *et al.*, 2008).

Results and Discussion

XRD analysis of the silt fractions (50-2 μm) of both the soils indicated the presence of smectite, vermiculite, chlorite, mica, kaolin, quartz and feldspar (Fig. 1). In the Seloo soils, silt fraction was dominated by smectites followed by quartz and feldspars and in Saikhindi soils silt fraction was dominated by smectites followed by feldspars and quartz.

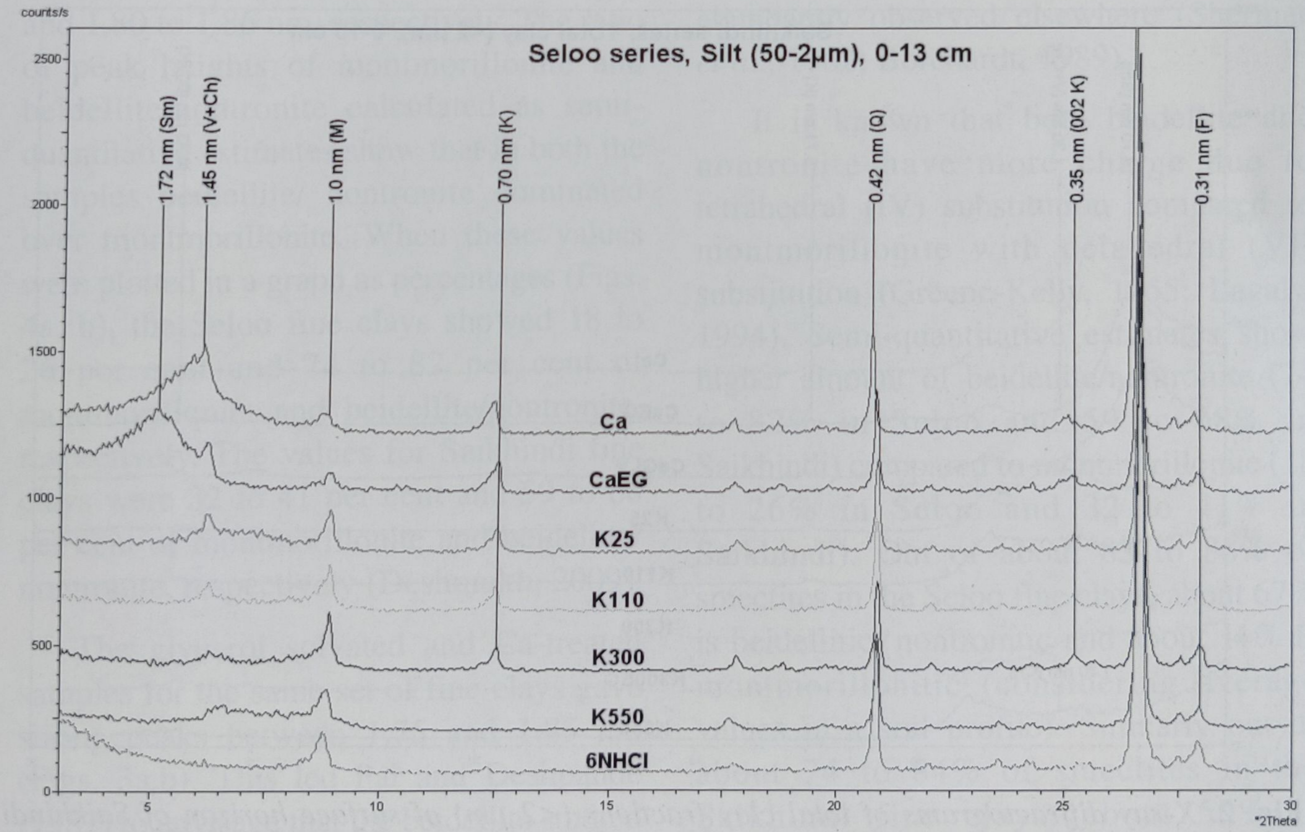


Fig. 1. *X-ray diffractograms of silt fractions (50-2 µm) of surface horizon of Seloo series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K-saturated and heated to 25, 110, 300, 550°C. 6NHCl = 6N HCl treated fine clays; Sm = Smectite, V + Ch = Vermiculite plus Chlorite; K = Kaolin; F = Feldspars; Q = Quartz.*

The total clay fractions (<2 μm) for both the soils are dominantly composed of smectite followed by small amounts of vermiculite, chlorite, mica and feldspars (Fig. 2). The fine clay fractions are mostly composed by smectite with small amounts of vermiculite and traces of chlorite, kaolin and feldspar (Figs. 3a,b). The smectite content was higher in fine clays of Seloo soils (83-88%) compared to Saikhindi (78-84%). The smectite was slightly chloritised as evidenced by the broadening of the peak towards the lower angle side of 1.0 nm peak in K-saturated sample after subsequent heating to 550°C. Such chloritization is common in black soils of the Peninsular India (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1993; Ray *et al.*, 2008). However, chloritization in smectites was relatively less in black soils under study compared to some other soils from Maharashtra (Kapse, 2007; Thakare, 2008; Bhople, 2010; Ray *et al.*, 2008).

Hofmann-KIemen effect (1950) modified by Greene-Kelly (1953) and Lim

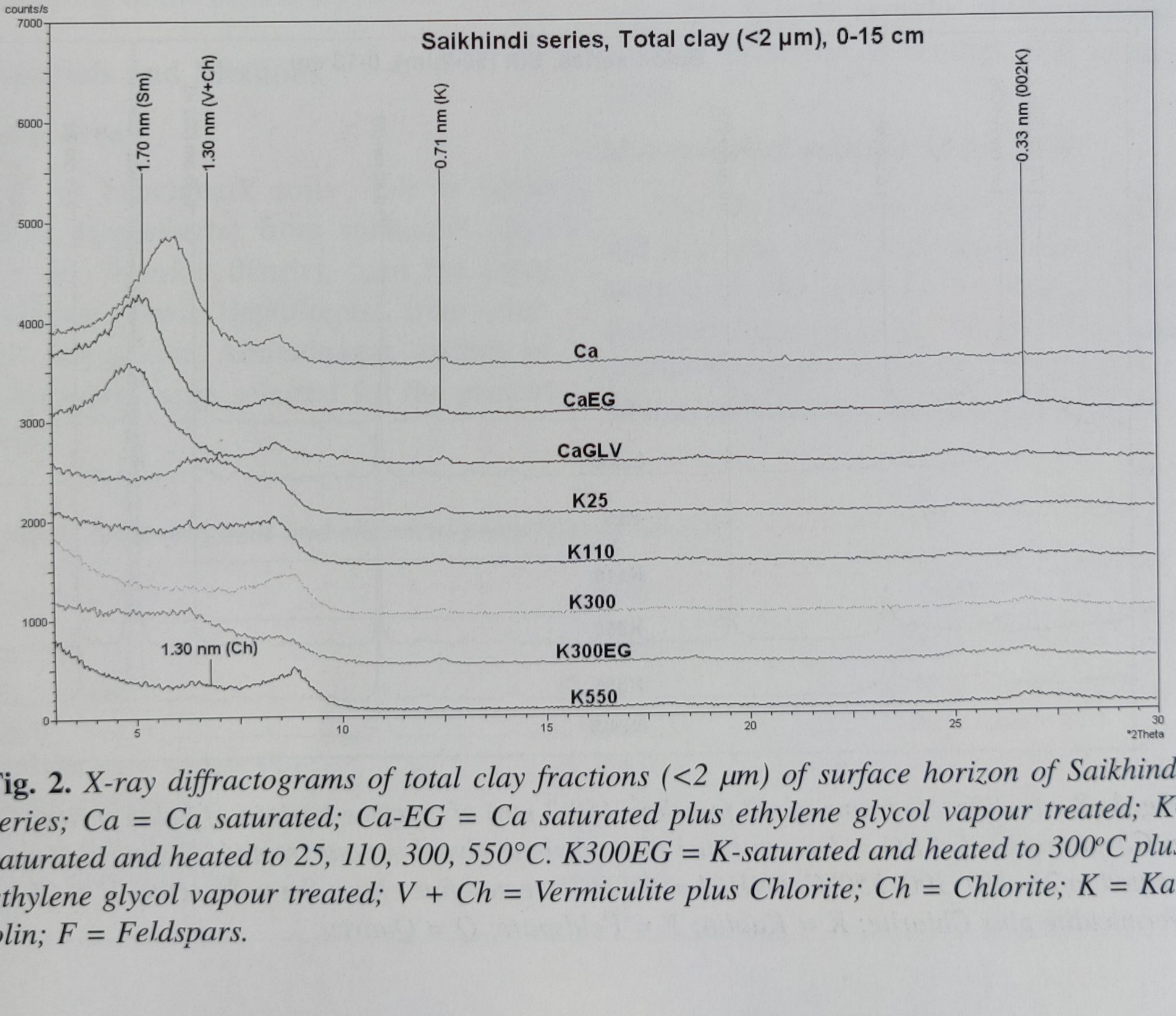


Fig. 2. *X-ray diffractograms of total clay fractions (<2 μm) of surface horizon of Saikhindi series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; V + Ch = Vermiculite plus Chlorite; Ch = Chlorite; K = Kaolin; F = Feldspars.*

and Jackson (1986) distinguishes between montmorillonite and beidellite by glycerol solvation of the Li-saturated and heated samples. Montmorillonite can be distinguished from beidellite/nontronite wherein Li-saturated samples when treated with glycerol, the former collapses to 0.95 nm and the latter expands to about 1.8 nm (Pal and Deshpande, 1987; Bhattacharyya *et al.,* 1993; Ray *et al.,* 2008). The soil fine clays in the present study shows the presence of both montmorillonite and beidellite/nontronite (Figs. 3a, b) as evidenced by the peaks at 0.95 to 1.00 nm and 1.80 to 1.86 nm, respectively. The ratio of peak heights of montmorillonite and beidellite/nontronite calculated as semi-quantitative estimates show that in both the samples beidellite/ nontronite dominated over montmorillonite. When these values were plotted in a graph as percentages (Figs. 4a, b), the Seloo fine clays showed 18 to 26 per cent and 74 to 82 per cent of montmorillonite and beidellite/nontronite, respectively. The values for Saikhindi fine clays were 32 to 41 per cent and 59 to 68 per cent of montmorillonite and beidellite/ nontronite, respectively (Deshmukh, 2009).

The glycerol solvated and Ca-treated samples for the same set of fine clays gave strong peaks between 1.75 and 1.85 nm (Figs. 3a,b). This led Pal and Deshpande (1987) to envisage that the beidellite studied by Harward *et al.* (1969) had apparently a higher tetrahedral charge than the fine clay smectites of Vertisols under study. In other words, fine clay smectite in these Vertisols is nearer to montmorillonite of the montmorillonite-beidellite series. They further logically stated that since the nontronite would behave similarly as beidellite does in Greene-Kelly test and the fine clay smectites studied is unstable to the HCl treatments releasing considerable iron, this mineral is nearer to the montmorillonite of the montmorillonite-nontronite series. Their study also highlights the importance and dominance of nontronite species in the shrink-swell soils of Peninsular India as otherwise not abundantly observed elsewhere (Sherman *et al*., 1962; Borchardt, 1989).

It is known that both beidellite and nontronite have more charge due to tetrahedral (IV) substitution compared to montmorillonite with octahedral (VI) substitution (Greene-Kelly, 1955; Lagaly, 1994). Semi-quantitative estimates show higher amount of beidellite/nontronite (74 to 82% in Seloo and 59 to 68% in Saikhindi) compared to montmorillonite (18 to 26% in Seloo and 32 to 41% in Saikhindi). Out of about 83 to 88% of smectites in the Seloo fine clays, about 67% is beidellitic/ nontronitic and about 11% is montmorillonitic (considering average values in a soil profile). Similarly out of about 74 to 84% of smectites in the Saikhindi fine clays, about 50% is beidellitic/ nontronitic and about 28% is montmorillonitic. The average layer charge determined by alkylammonium method for

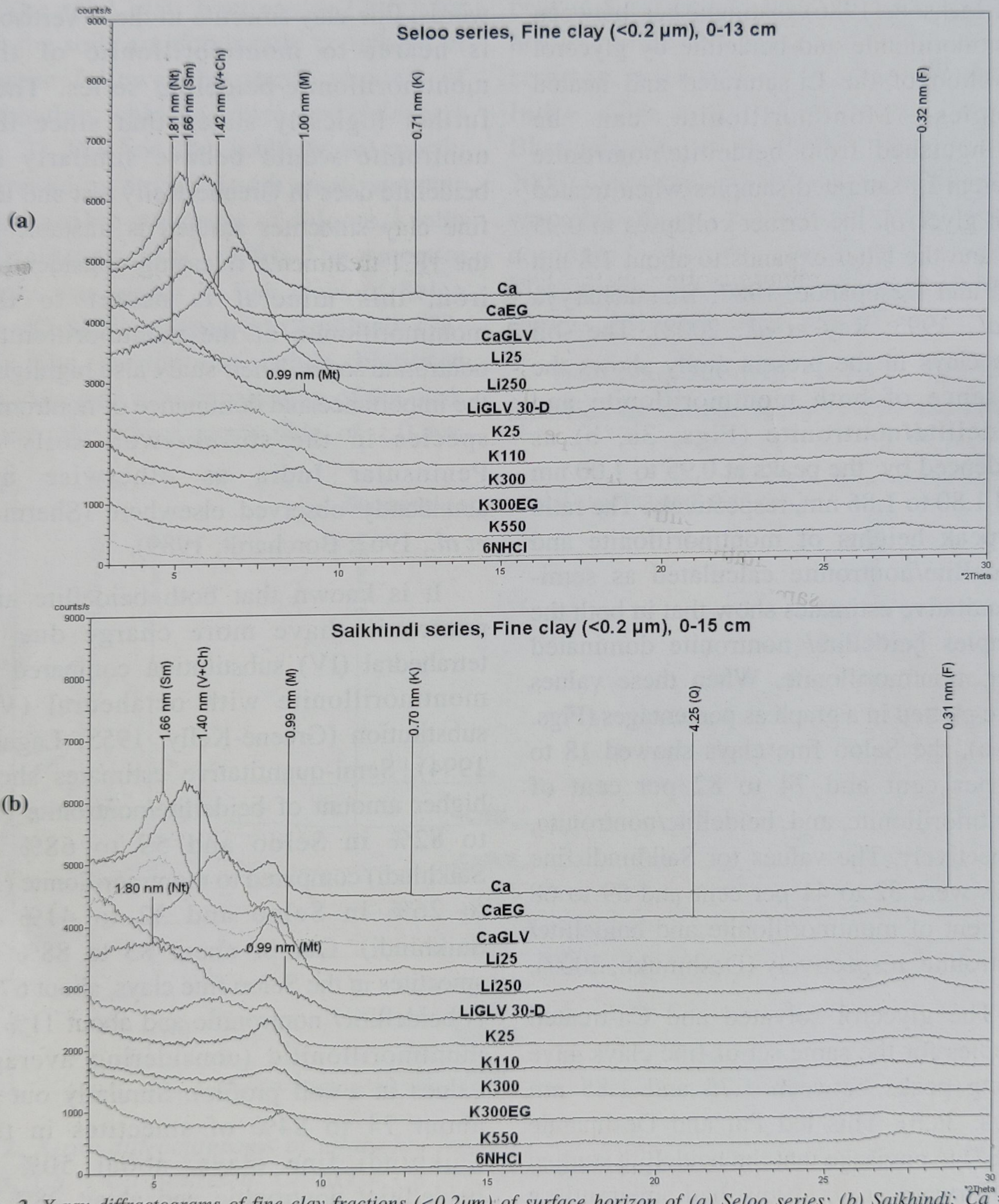
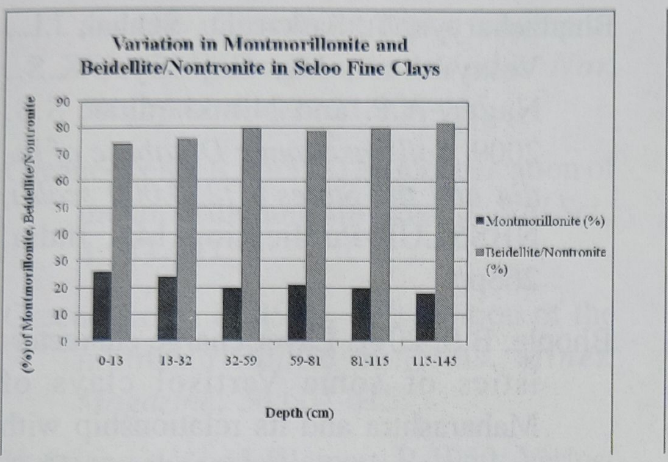


Fig. 3. *X-ray diffractograms of fine clay fractions (<0.2µm) of surface horizon of (a) Seloo series; (b) Saikhindi; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; CaGLV = Ca-saturated plus glycerol vapour treated; Li = Li-saturated and heated to 25°C, 250°C (16h), LiGLV 30-D = Li-saturated and heated at 250°C plus glycerol vapour treated and scanned after 30 days; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; 6NHCl = 6N HCl treated fine clays; Sm = Smectite, B/N = Beidellite/Nontronite; V + Ch = Vermiculite plus Chlorite; M = Mica; Mt = Montmorillonite; K = Kaolin; F = Feldspars.*



(a) (b)

Fig. 4. *Semi-quantitative estimates of Montmorillonite and Beidellite/Nontronite in (a) Seloo (b) Saikhindi fine clays.*

Seloo and Saikhindi fine clays are 0.472 and 0.431 mol(-)/ $(Si,Al)_4O_{10}(OH)_2$, respectively (Deshmukh, 2009). Moreover, the vermiculite content (6 to 8% in Seloo and 6 to 7% in Saikhindi) and amount of hydroxy-interlayering (Ray *et al.*, 2008; Deshmukh, 2009) in both the soil fine clays are comparable and contributions towards higher charge due to these minerals would be almost identical. Therefore, higher tetrahedral substitution due to higher values of beidellite/ nontronite species in fine clay smectites of Seloo resulted in higher charge compared to Saikhindi (Deshmukh, 2009). This feature is generally repetitive for other soil fine clays (Thakare, 2008; Ray *et al.*, 2008; Bhople, 2010).

Low charge dioctahedral smectites (beidellite/nontronite and montmorillonite, confirmed based on XRD with diagnostic analytical methods, Pal *et al.*, 1987; Bhattacharyya *et al.*, 1993) are known to be a direct weathering product of plagioclase feldspars (Pal and Deshpande, 1987) under humid tropical climate (Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). The difference in the amounts of beidellite/ nontronite species of smectites in the two soil fine clays of two distinct agro-ecoregions may be due to the differential loading of clay smectite during the erosion-deposition episodes of the weathering products of the Deccan basalt in the geological past (Pal and Deshpande, 1987). Due to their low charge these two smectite species may not have any implications in K adsorption of these soils (Pal *et al.*, 2012) like those derived from micas (Singh and Heffernan, 2002). Thus the K adsorption by these soils is due to the presence of vermiculite as reported earlier (Pal *et al.*, 2012).

Conclusions

Both the soil fine clays showed higher values of beidellite/nontronite compared to montmorillonite species of smectite. Larger amounts of beidellite/nontronite with relatively higher charge may apparently suggest their greater capacity to adsorb/ fix potassium compared to montmorillonite as reported often in the literature. This is in contrast with the established fact that low charge fine clay smectites do not show K-selectivity properties. This fact demands fresh research initiatives to find a probable answer for a consistent report of K response (through external K fertilizer addition) even though the soil test values showed high available K in the shrink-swell soils of the Peninsular India.

Acknowledgement

The authors are grateful to the Director, NBSS&LUP for providing the necessary facilities for the work. They are also thankful to Mr. S.P. Chivane for providing the Seloo soil samples and Ms. D.V. Balbuddhe and Mrs. W. Khandwe for word processing the manuscript.

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(Received June, 2012; Accepted November, 2012)

Clay Research, Vol. 31, No. 2, pp. 94-108 (2012)

Role of Calcium Carbonate Minerals in Improving Sustainability of Degraded Cracking Clay Soils (Sodic Haplusterts) by Improved Management: An Appraisal of Results from the Semi-Arid Zone of India

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Abstract: *A long-term heritage experiment (LTHE) following the improved management (IM) system was initiated in 1976 on bench mark Vertisols (Kasireddipalli soils, Sodic Haplusterts with ESP > 5 but < 15 and saturated hydraulic conductivity, sHC < 10 mm hr^{-1}) under semi-arid tropics (SAT) environments at International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) centre, Patancheru, India for increased productivity. It was undertaken to test the hypothesis that the IM system in combination with appropriate cropping practices can improve soil quality in comparison to the prevailing traditional management (TM) practices. The average grain yield of the IM system over thirty years was five times more than that in the TM system. Adaptation of the IM system improved physical, chemical and biological properties of soils to the extent that Sodic Haplusterts now qualify for Typic Haplusterts. Constant release of higher amount of Ca^{2+} ions during the dissolution of $CaCO_3$ (8.4 mg/100g soil/year in 1m profile) under the IM system, compared to slower rate of formation of $CaCO_3$ (0.10 mg/100g soil/year in 1m profile), provided soluble Ca^{2+} ions enough to replace unfavourable Na^+ ions on the soil exchange sites. Higher exchangeable Ca/Mg ratio in soils under IM system improved the sHC for better storage and release of soil water during dry spell between rains. Adequate supply of soil water helped in better crop productivity and higher organic carbon (OC) sequestration. The improvement in Vertisols' sustainability suggests that the IM system is capable of mitigating the adverse effect of climate change, and the sustainability of the Typic Haplusterts may continue for another couple of centuries under SAT environments, and thus stands for its adaptation on a sufficiently large scale through national and international initiatives.*

Key words : $CaCO_3$, Improved management, ICRISAT, Vertisols' sustainability, SAT, Climate change, Mitigation

Sustainable development meets the needs of the present without compromising the ability of future generations to meet their own needs for land (W C E D, 1987). Smith and Powlson (2003) adapted this definition to derive a definition for

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sustainable soil management. They defined soil management that meets the needs of the present without compromising the ability of future generations to meet their own needs from that soil. Thus, soil management is sustainable when it does not alter the capacity of the soil to provide for future needs. Soil sustainability can be threatened by a numerous management practices; including over-cultivation, decreased or increased water abstraction, under-fertilisation or over-fertilisation, careless use of biocides, failure to maintain soil organic matter levels and clearing natural vegetation. These may threaten sustainability in a number of ways; through physical and chemical processes (eg. by increasing soil erosion, salinisation, desertification), or biological processes (eg. by decreasing soil fertility). When soil management is poor, soil sustainability is often threatened by a combination of these factors at the same time (Smith and Powlson, 2003). Climate change may further increase the threat to soil sustainability in poorer countries because cereal crop yields are predicted to decline in most tropical and sub-tropical regions under future climates (Rosenzweig and Parry, 1994, Fischer *et al.*, 2001), in countries which have a low capacity to adapt (IPCC, 2007). The impact of climate change in soils of tropical parts of Indian subcontinent in particular and in the world in general, in terms of impairment in their physical, chemical and biological properties has attracted the attention of soil researchers in recent years (Pal *et al.*, 2009a, b).

Amidst neotectonics and the global warming phenomenon, rising temperature and shrinking annual rainfall with erratic distribution pose perpetual threats for soils not only for the Indian subcontinent but also for soils of similar climatic conditions elsewhere (Pal *et al.*, 2009b). In India, a change of climate has been recorded from humid to semi-arid in rainfed areas only during the Holocene period (Pal *et al.*, 2001; 2009a). It is observed that the major soil types of India under SAT environments are becoming calcareous with the concomitant development of exchangeable sodium percentage (ESP) in the subsoil, which indicates a climatically controlled natural degradation (Pal *et al.*, 2000). This type of degradation ultimately modifies the soil physical and chemical properties. Such modifications resulting from regressive pedogenesis (Johnson and Watson-Stegner, 1987) restrict the entry of rain water, and reduce the storage and release of soil water (Kadu *et al.*, 2003). The lack of soil water impairs the possibility of growing both rainy and winter crops in a year, especially in vast areas under Vertisols of SAT with mean annual rainfall (MAR) <1000mm (Pal *et al.*, 2011). This way not only the Vertisols with ESP>15 (Sodic Haplusterts) but also the soils with ESP >5 but <15 (Aridic Haplusterts) cease to be sustainable for growing agricultural crops under SAT environments (Pal *et al.*, 2009b, 2011). Thus, the loss of soil sustainability may not be always due to the human-induced soil degradation process (Oldeman, 1994).

The Vertisols in the ICRISAT heritage watersheds at Patancheru ($17^0 36$ N, 78^0 16 E, 545 m altitude) belong to Kasireddipalli series and was initially classified as Typic Pellusterts (Murthy *et al.*, 1982) but is revised to Sodic Haplusterts recently in view of their very low sHC (< 10 mm hr^{-1}) that causes decline in crop yield more than 50% as compared to Typic Haplusterts of SAT environments (Pal *et al.*, 2003, 2006). The area receives 800 mm average annual rainfall; the average minimum temperature is 19^0 C and maximum temperature is 32^0C.

In SAT agro-ecosystems, the primary constraint for productivity is water. The study on the sustainability of Vertisols through adoption of integrated catchment management was started at the ICRISAT, Patancheru, Andhra Pradesh, India, since 1976. Two long term catchment heritage experiments (adjacent to each other) were studied with two systems (improved and traditional) with objectives to validate the hypothesis that improved management (IM) system of Vertisol not only enhances crop productivity, but also favours organic carbon (OC) sequestration and enhances soil quality (Wani *et al.*, 2003, 2007).

Description of Long-Term Heritage Experiments (LTHEs)

Improved system (IM): An integrated watershed management system with a broad-bed and furrow (BBF) landform treatment (El-Swaify *et al.*, 1985) was followed. The beds were 1.05 m wide with a 0.45 m furrow prepared at 0.4-0.6 % gradient using a bullock-drawn bed-marker mounted on a tropicultor (El-Swaify *et al.*, 1985). The land was refreshed soon after harvesting of the post-rainy season crop and after unseasonal rains the beds were formed again at the same place. Field traffic was confined to the furrows. Excess rainfall drained along the furrows and discharged into grassed waterways. Improved high-yielding varieties were dry-sown on a bed with a spacing of 1.5× 0.15 m for pigeon pea (*Cajanus cajan)* ICP1-6, 0.9 x 0.1 m for sorghum (*Sorghum bicolour*) CSH 9, and 0.75× 0.20 m for maize (*Zea mays*) DH 103 at a depth of 50-70 mm during the period 8-15 June each year. Sixty kg N ha^{-1} and 20 kg phosphorus (P_2O_5) ha^{-1} as urea and di-ammonium phosphate (DAP), respectively, were applied in rows with a seed and fertilizer drill. Generally, monsoon rains arrives on or after 15 June at Patancheru.

From 1976 to 1988 the field was treated as a single plot. A two-year rotation was followed with sorghum intercropped with pigeon pea (2:1 proportion) and maize during the rainy season followed by chickpea (*Cicer arietinum*) (Annigeri) in the post-rainy season. The field was divided from 1989 to 1998 in two plots and a two-year rotation with sorghum ICSV 745 intercropped with green gram (*Vigna radiata*) PS 16 in the rainy season followed by sorghum M 35-1 in the post-rainy season. The plots were treated as mirror images. Weed control was carried out by mechanical weeding once, using the tropicultor, and two hand weeding. Appropriate pest and disease management protocols were followed as required. Sorghum was harvested by cutting the plants at 150 mm from ground level, leaving the stubbles in the field. The stalks were dried and the plant dry matter weight was recorded. Pigeon pea was harvested at the end of February. In each plot from two replicates, an area of 12 m^2 from each replicate was used for recording yield parameters. Immediately after the harvest of pigeon pea, the land was cultivated and once in two years ploughed and left fallow. When summer rains occurred, the beds were reshaped for sowing of the next rainy season crops.

Traditional system(TM): The land was left as cultivated bare fallow from 1976 to 1988 during the rainy seasons and sorghum was grown as sole crop in the post- rainy seasons. From 1989 the field was divided in to two plots, with a two-year rotation of bare fallow/sorghum (M 35-1) followed by bare fallow/chickpea (Annigeri) in the next year. The two plots were treated as mirror images. Seeds were sown with a local seed drill on a flat surface when seedbed moisture was adequate. No inorganic fertilizers were applied to the crop, but 10 t ha^{-1} of farm yard manure (FYM) was broadcast each alternate year before land preparation. Sorghum was intercultivated once, and then hand weeded. The land was ploughed every two years; harrowing was done with a blade harrow to control weeds. Dry matter yields were recorded each year.

Results of the LTHEs

The updated results from the LTHEs (Fig.1) indicate that the moving average grain yield under the IM system over 30 years has been 5.1t ha^{-1} yr^{-1}. And this yield is nearly five-fold higher than under the TM system, which has an average yield of about 1.1t ha^{-1} yr^{-1}. The annual gain in yield in the IM system was 82 kg ha^{-1} as compared to 23 kg ha^{-1} in the TM system (Table 1). Enhanced crop productivity in the IM system increased its carrying capacity as compared to that in the TM system (21 persons ha^{-1} in the IM versus 4.6 persons ha^{-1} in the TM system) (Wani *et al.*, 2009). The yield of deep-rooted crops on Vertisols under rain-fed conditions depends primarily on the amount of rain stored in the profile, and its release during crop growth. The IM system thus shows increased rainwater use efficiency as compared to the TM system (65% versus 40%) (Table1). In addition, it shows reduced runoff (from 220 mm to 91 mm) and soil loss as a result of implementation of the IM (from 6.64 t ha^{-1} to 1.6 t ha^{-1}) (Table 1) (Wani *et al.*, 2003). The favourable entry of rain water has been possible because of enhancement in sHC values > 10 mm hr^{-1}(weighted mean in 1m

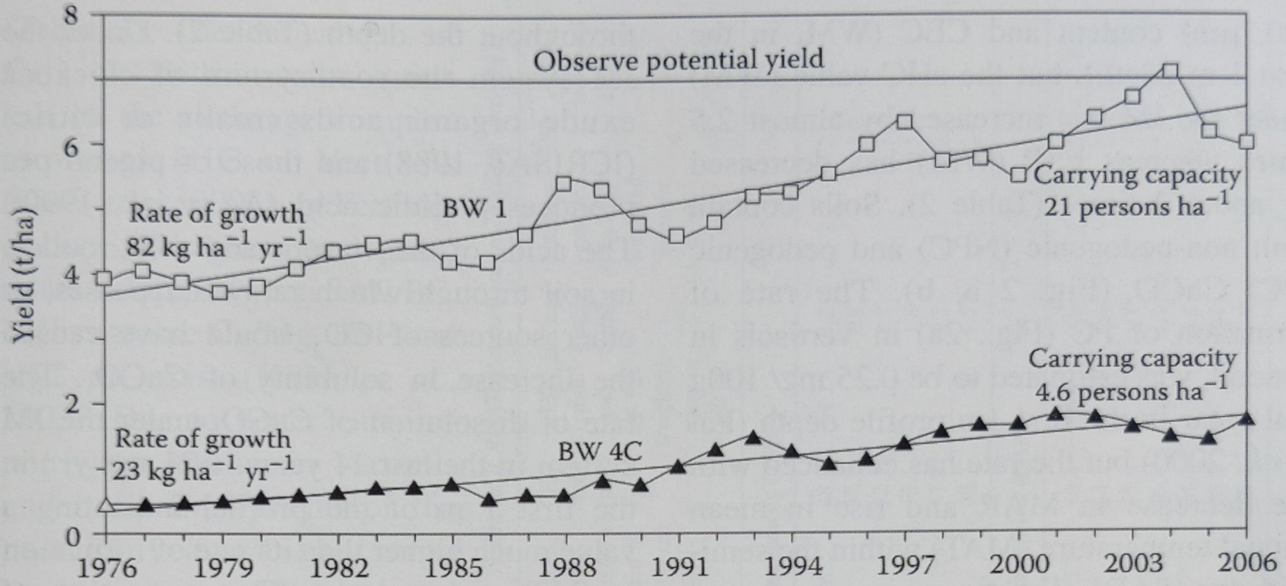


Fig. 1. *Three year moving average of sorghum and pigeonpea grain yields under IM and TM in Kasireddipalli soils at Patancheru, India. Adapted from Wani et al.(2007).*

Table 1. *Effect of 24 years of LTE on the grain yield, SOC and total Nitrogen, microbial biomass C (MBC), microbial biomass N (MBN), and P in Vertisols (Kasireddipalli series) **

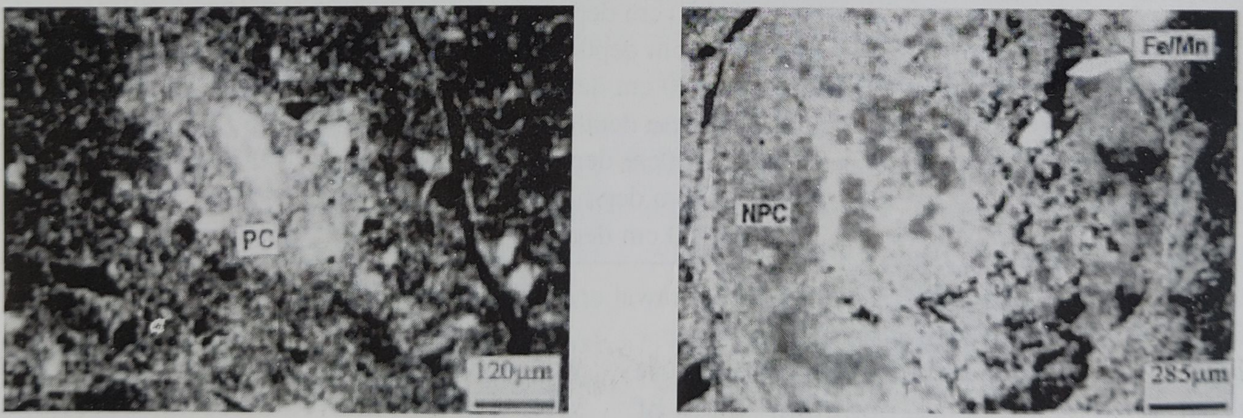
Grain yield/soil properties	Improved management (IM)	Traditional management (TM)
Grain yield	5.1 t ha $^{-1}$ yr $^{-1}$	1.1 t ha $^{-1}$ yr $^{-1}$
OC (t ha $^{-1}$)	27.4 (0-60 cm depth)	21.4 (0-60 cm depth)
	19.4 (60-120 cm depth)	18.1 (60-120cm depth)
Total N (kg ha $^{-1}$)	2684 (0-60 cm depth)	2276 (0-60 cm depth)
	1928 (60-120 cm depth)	1884 (60-120 cm depth)
MBC (kg C ha $^{-1}$)	2676 (0-60 cm depth)	1462 (0-60 cm depth)
	2137 (60-120cm depth)	1088 (60-120 cm depth)
MBN(kg N ha $^{-1}$)	86.4 (0-60 cm depth)	42.1 (0-60 cm depth)
	32.2 (60-120 cm depth)	25.8 (60-120 cm depth)

* Adapted from Wani *et al.* (2003; 2007), Sahrawat *et al.* (2010) and Pal *et al.* (2011)

depth, WM) in soils of the IM system (Table 2). It is a fact that an optimum yield of deep-rooted crops (cotton) in Vertisols of SAT of central India can be obtained when the soils are non-sodic (ESP<5) with sHC ≥ 20 mm hr^{-1}, and 50% reduction in yield was observed in Vertisols with ESP>5 and sHC <10 mm hr^{-1} (Kadu *et al.*, 2003; Pal *et al.*, 2006).

Vertisols under IM and TM system have comparable clay (<2μm), and fine clay

(<0.2μm) content and CEC (WM, in the first 1 m depth), but the sHC value (WM) under the IM has increased by almost 2.5 times whereas ESP (WM) has decreased by about 2 times (Table 2). Soils contain both non-pedogenic (NPC) and pedogenic (PC) $CaCO_3$ (Fig. 2 a, b). The rate of formation of PC (Fig.. 2a) in Vertisols in general, was estimated to be 0.25 mg/ 100g soil /year in the first 1m profile depth (Pal *et al*., 2000) but the rate has enhanced with the decrease in MAR and rise in mean annual temperature (MAT) within the semi-arid dry (SAD) climatic environments and it can be more than 1.0 mg/100g soil /year (Pal *et al.*, 2006). The $CaCO_3$ content (WM) of the IM system was 5.7% whereas it remained at 6.2% under the TM system. The depth distribution of $CaCO_3$ in soils under the IM system indicates a gradual increase and under the TM system its amount has remained almost same throughout the depth (Table 2). Under the IM system the root system of chickpea exude organic acids (malic or citric) (ICRISAT, 1988) and those of pigeon pea produces piscidic acid (Ae *et al.*, 1990). The acids of these crops and their rootlets in soil through which rainwater passes, or other sources of CO_2, could have caused the increase in solubility of $CaCO_3$. The rate of dissolution of $CaCO_3$ under the IM system in the last 24 years is 21 mg yr^{-1} in the first 1 m of the profile, indicating a value much higher than its rate of formation in SAT environments. The proportion of Ca to C in $CaCO_3$ is more than 3.0, suggesting the availability of Ca ions in soil solution is higher (8.4 mg/100g soil/ year in 1m profile) than that of bicarbonate ions (2.52 mg/100g soil/year in 1m profile). The favourable amount of Ca^{2+} ions leads to an increase in exchangeable Ca/Mg ratio and a concomitant decrease in ESP



(a) (b)

Fig. 2. *Micromorphological features of $CaCO_3$ in Kasireddipalli soils, in cross-polarized light. (a) PC as diffuse nodules and as micrite crystals in the ground mass, (b) NPC showing dissolution. Adapted from Pal et al.(2003).*

(Table 2). The enrichment of Ca^{+2} ions both in soil solution and on the exchange complex improves sHC of Vertisols (Kadu *et al.*, 2003). In Vertisols of the SAT regions, pedogenic relationships between SAT, PC, exchangeable Ca/Mg, ESP and sHC do exist (Kadu *et al.*, 2003). Due to better entry of rain water and air in Vertisols under the IM system for the past 24 years, higher crop productivity was observed, and thus Vertisols sequestered more amount of OC in the first 0.3m depth of the profile than in the soil under the TM system. At present, soils under the IM system contain 0.53 % OC (WM) whereas soils under TM system contain 0.42% (Table 2). The rate of addition of OC for the last 24 years since 1977 has been 5 mg yr^{-1} in the first 1m of the Vertisols under the IM system. Increased OC sequestration in soils of the tropics induces dissolution of native $CaCO_3$ and its leaching (Bhattacharyya *et al.*, 2001). The improvement in physical and chemical environments highlight the role of $CaCO_3$ that remains chemically inert in Vertisols (Pal *et al.*, 2000) during its sequestration

Table 2. *Modification of physical and chemical properties of Vertisols through improved management system at ICRISAT, Patancheru in 24 years since 1977.*

Horizon	Depth cm	Clay %	Clay (%), weighted of man in 0-100 cm	Fine clay %	Fine clay (%), weighted mean in 0-100 cm	sHC mm hr-1	sHC mm hr-1, weighted mean in 0-100 cm	pH H_2O (1:2)	Organic carbon %	Organic carbon (%) weighted mean in 0-100 cm	Ca CO_3 %	$CaCO_3$ (%), weighted mean in 0-100 cm	CEC cmol (p+) kg-1	CEC (cmol (p+) kg-1), weighted mean in 0-100 cm	Exchan- geable Ca/Mg	Exchan- geable Ca/Mg, weighted mean in 0-100 cm	ESP	ESP weighted mean in 0-100 cm
Kasireddipalli Soil (Sodic Haplusterts) under Traditional Management (TM)[a]																		
Ap	0-12	48.0	53.0	26.4	33.0	7.0	4.0	7.8	0.6	0.42	6.0	6.2	48.7	52.2	3.2	2.2	2.0	8.3
Bw1	12-30	51.4		29.7		6.0		7.8	0.4		6.2		52.1		2.8		4.0	
Bss1	30-59	52.5		32.5		6.0		8.1	0.4		6.0		52.2		2.1		7.1	
Bss2	59-101	55.6		36.4		2.0		8.5	0.4		6.4		53.5		1.8		13.0	
Bss3	101-130	59.4		30.8		2.0		8.5	0.4		6.5		57.8		3.1		8.0	
BCk	130-160	58.0		38.7		1.0		8.2	0.1		9.1		49.5		1.5		22.2	
Kasireddipalli Soil (Typic Haplusterts) under Improved Management (IM)[b]																		
Ap	0-12	52.1	54.7	28.8	32.8	17.0	11.0	7.5	1.0	0.53	4.2	5.7	50.4	56.0	2.9	2.4	2.0	4.5
Bw1	12-31	51.5		28.1		16.0		7.8	0.6		4.5		54.3		2.4		2.0	
Bss1	31-54	54.2		34.0		10.0		7.8	0.4		6.2		55.6		1.7		3.0	
Bss2	54-84	57.3		40.0		9.0		8.2	0.4		5.1		56.4		1.9		7.0	
Bss3	84-118	56.5		26.0		7.0		8.1	0.5		8.6		61.6		3.8		7.0	
Bss4	118-146	59.3		31.7		3.0		8.2	0.5		8.4		58.2		2.1		7.0	
BC	146-157	60.0		41.5		—		8.2	0.3		7.4		55.2		1.1		9.0	

[a]Adapted from Pal *et al.* (2003); [b]Adapted from Bhattacharyya *et al.* (2007)

(Sahrawat, 2003), but acts as a soil modifier during the adaptation of the IM system. The improvement in soil properties is also reflected in classification of Vertisols. The Kasireddipalli soils of the TM system (Sodic Haplusterts) now qualify for Typic Haplusterts under the IM system (Pal *et al*., 2011).

It is observed that along with the increased crop productivity, OC, total N, and Olsen P also increased. Among the soil biological properties, microbial biomass carbon (MBC), and microbial biomass N (MBN) also increased in the improved physical and chemical environments of Vertisols under the IM system (Table 1).

Discussion

Amidst climate change from humid to semi-arid in Indian Peninsular region during the Holocene period, sequestration soil inorganic carbon (PC) in SAT environments (Fig. 2a) due to the dissolution of NPC (Fig. 2b) is the prime chemical reaction responsible for the increase in pH, the decrease in Ca/Mg ratio of exchange site with depth and the development of subsoil sodicity in Vertisols (Table 2)(Srivastava *et al.,* 2002). These modifications in soil chemical properties together impair the hydraulic properties of soils, which restrict the entry of air and rain water in subsoil region of the profile. Thus, Vertisols of the TM system with ESP>5 and <15, and sHC < 10 mm hr^{-1}, show poor crop productivity due to inadequate amount of soil water available during crop growth (Fig.1). Recently Kadu *et al.*(2003) made an attempt to identify bio-physical factors that limit the yield of deep-rooted crops (cotton) in 29 Vertisols, developed in the basaltic alluvium of sub-humid dry (SHD) to semi-arid dry (SAD) climate of Nagpur (SHD), Amravati (SAD) and Akola (SAD) districts of Vidarbha region of Maharashtra (adjacent state to Andhra Pradesh) in central Peninsular India. They have demonstrated that with the decrease in MAR and increase of MAT, the physical, chemical and biological properties of Vertisols of Amravati and Akola districts under SAD climates are degraded as soils lose OC and become more calcareous, alkaline and sodic due to accelerated formation of PC. As a result, the sHC of soils have decreased and impaired the cotton productivity (Table 3). The AWC (available water content) calculated on the basis of moisture content held between 33 and 1500kPa (Table 3), indicate that not only the Typic/Aridic Haplusterts but also the Sodic Haplusterts can hold sufficient water apparently for optimum crop growth. But a non-significant negative correlation between yield of cotton and AWC (Table 4) indicates that during the growth of crops this water is not released because of prevalence of Na^+ ions on exchange sites of Aridic Haplusterts and Sodic Haplusterts with ESP > 5. In fact, storage of soil water in the subsoils is governed by the movement of water in the profile. The sHC of Vertisols of SAT, decreases rapidly with depth, and the

Table 3. *Range in values of AWC, OC, PC, ESP, sHC and yield of cotton in Vertisols of Vidarbha, Central India*

District, Vidarbha Region, Maharashtra, Central India	Soil Classification	AWC(%)[1]*	OC (%)[2]	PC (%)[3]*	ESP[4]*	sHC[5]* (mm hr^{-1}) weighted mean in the profile (1 m)	Cotton yield (t ha^{-1}) (seed+lint)*
Nagpur (MAR – 1011 mm)	Typic Haplusterts/ Typic Calciusterts	14-20	0.74	3 – 6	0.5 – 11	4 – 18	0.9 – 1.8
Amravati (MAR – 975 mm)	(a) Aridic Haplusterts	10-20	0.54	3 – 7	0.8 – 4	2 – 19	0.6 – 1.6
	(b) Sodic Haplusterts	17-24	0.42	3 – 13	16 – 24	0.6 – 9.0	0.2- 0.8
Akola (MAR – 877 mm)	(a) Aridic Haplusterts	17	0.30	3.6	7 – 14	3 – 4	0.6-1.0
	(b) Sodic Haplusterts	18	0.20	4.0	19 – 20	1- 2	0.6

AWC= available water content (weighted mean in 1m depth of soil), [2]OC= organic carbon (weighted mean in 1m depth of soil), [3]PC=pedogenic $CaCO_3$ (weighted mean in 1m depth of soil), [4]ESP=exchangeable sodium percentage (sodicity)(maximum value in 1m depth of soil), [5]sHC= saturated hydraulic conductivity (weighted mean in 1m depth of soil). * minimum and maximum average values. Adapted from Kadu *et al.* (2003).

decrease is sharper in Aridic/Sodic Haplusterts with ESP >5 (Pal *et al.*, 2009a). This is observed by a significant positive relation between ESP and AWC, also by a significant negative correlation between yield and ESP (Table 4). A significant positive correlation between yield and exchangeable Ca/Mg (Table 4) indicates that a dominance of Ca^{2+} ions in the exchange sites of Vertisols is required to improve the hydraulic properties for a favourable yield of crop. The development of subsoil sodicity (ESP ≥ 5) replaces Ca^{2+} ions in the exchange complex, causes reduction in yield of cotton in Aridic /Sodic Haplusterts (ESP ≥ 5). A significant negative correlation between ESP and exchangeable Ca/Mg (Table 4) indicates impoverishment of soils with Ca^{2+} ions during the sodification process. This process causes the depletion of Ca^{2+} ions from the soil solution in the form of $CaCO_3$ with the concomitant increase of ESP with pedon depth (Balpande *et al.*, 1996; Vaidya and Pal, 2002). Thus, these soils show the presence of PC (Pal *et al.*, 2000; Srivastava *et al.*, 2002; Vaidya and Pal, 2002). This chemical process is evident from the positive correlation between ESP and carbonate clay (PC) (Table 4). A significant positive correlation between yield of cotton and carbonate clay (Table 4) indicates that like ESP, the formation of PC is also a yield-reducing factor and a more important soil parameter than total $CaCO_3$ (PC+NPC) in soils (Sys *et al.*, 1993; NBSS&LUP, 1994). Due to an accelerated rate of formation of PC in dry climates, the hydraulic properties of Vertisols are impaired and thus, a significant negative correlation exits between ESP and sHC (Kadu *et al.*, 2003; Pal *et al.*, 2006). All the processes operating in soils of dry climates also influence the sHC of the Vertisols and thus, a significant positive correlation exits between yield of cotton and sHC (Table 4). Thus, Kadu *et al.* (2003) in view of pedogenetic processes that ultimately impair the hydraulic properties of soils advocated the evaluation of Vertisols (without any soil modifiers like Ca-zeolites and gypsum, Pal *et al.*, 2006) for deep-rooted crops on the basis of sHC alone.

The results of LTHE on Kasireddipalli soils (Sodic Haplusterts) under the IM system involving legumes, BBF land and water management protocols, use of inorganic fertilizers, indicate that physical, chemical and biological properties of Kasireddipalli soils can be improved to a great extent and can also convert the naturally degraded Vertisols in to resilient ones. This fact is evident from their much higher crop productivity and carrying capacity as compared to Vertisols (Sodic Haplusterts) of the LTHE under the TM system with crop rotation involving rainy season bare fallow and addition of organic fertilizers like FYM. Release of good amount Ca^{2+} ions during the dissolution of $CaCO_3$ (8.4 mg/100g soil/year in 1m

Table 4. *Co-efficient of correlation among various soil attributes and yield of cotton* [1]

No.	Parameter Y	Parameter X Based on 29 Vertisols	r
1	Yield of cotton (q ha^{-1})	AWC (%) WM [b]	-0.10
2	Yield of cotton (q ha^{-1})	ESP max [a]	- 0.74*
3	Yield of cotton (q ha^{-1})	sHC WM [b]	0.76*
4	Yield of cotton (q ha^{-1})	carbonate clay [c]	-0.64*
5	Yield of cotton (q ha^{-1})	Exch. Ca/Mg WM [b]	0.50*
6	ESP max [a]	AWC (%) WM [b]	0.30*
7	ESP max [a]	Exch. Ca/Mg WM [b]	-0.55*
8	ESP max[a]	clay carbonate [c]	0.83*

[1]Adapted from Kadu *et al.* (2003)

[a]Maximum in pedon; [b]weighted mean; [c]fine earth basis

AWC, available water content; ESP, exchangeable sodium percentage; sHC, saturated hydraulic conductivity.

*Significant at 1% level.

profile) under the IM system compared to immobilization of Ca^{2+} ions during formation of $CaCO_3$ (0.10 mg/100g soil/year in 1m profile) caused the improvement of sHC for storage and release of soil water during dry spell between rains in the growing season. Adequate supply of soil water helped in better crop productivity, and higher OC sequestration, indicating that soil chemistry is seldom visible in maintaining soils' sustainability (Buol, 1995). Improvement in sHC in the subsoil through the IM system helping in storage and release of soil water during crop growth suggests that it may also work successfully even in calcareous Vertisols with ESP < 5 (Typic Haplusterts), wherein sHC also decreases rapidly with depth (Balpande *et al.,* 1996; Pal *et al*., 2003, 2006). The resilience of Sodic Haplusterts through the management interventions under the IM system of ICRISAT clearly suggests that the IM system is capable of mitigating the adverse effect of climate change of the Indian Peninsula. Thus, the IM system can be considered as good (IPCC, 1997, Paustian et al., 1997) or recommended (Lal, 2010) practices. The sustainability of IM system would, however, depend upon the maintenance of Vertisols' sustainability as Typic Haplusterts with time in SAT environments. The continuance of agronomic practices of the IM system can supply the most important Ca^{2+} ions both in solution and exchange sites of soil and such chemical environment would not allow Typic Haplusterts (still containing 5.7% $CaCO_3$, Table 2) to transform to any other soil order so long $CaCO_3$ (both PC and NPC) would continue to act as a soil modifier (Pal *et al.,* 2011). For complete dissolution of 5.7% $CaCO_3$ 'at the rate of' 21mg/100g soil/year, the IM system would require for more than 250 years. Thus, Typic Haplusterts are expected to be sustainable for another couple of centuries.

Despite this fact that the IM system is a cost-effective and win-win technology to improve the crop productivity in Vertisols under SAT environment, its full potential has neither been realised nor has been adapted on a sufficiently large scale to have substantial impact (Wani et al., 2007). A fresh initiative is warranted for the implementation of the IM technology to make Sodic Haplusterts resilient and sustainable by providing incentives, technological know-how, required resources and policy support to the farmers through transferable C credits under CDM of the Kyoto Protocol as C sequestration is one the important mitigation strategies to cope with the impacts of climate change (Lal, 2004). Trading C credits is a good incentive in improving the quality of soil and environments, and restoring the degraded ecosystem in addition to enhancing farm income (Lal, 2005).

Conclusions

SAT induced naturally degraded Vertisols of the Holocene period (with ESP>5, but <15 and sHC < 10 mm hr^{-})

like Kasireddipalli and similar soils (Sodic Haplusterts, without soil modifiers like Ca-zeolites and gypsum) occurring elsewhere show poor crop productivity. The IM system of ICRISAT when adapted in such soils can make Sodic Haplusterts resilient by converting them to Typic Haplusterts. In view of constant supply of soluble Ca^{2+} ions through the dissolution of $CaCO_3$, sustainability of still calcareous Typic Haplusterts can be maintained for couple of centuries under SAT environments. Therefore, the IM system can be considered as a good/recommended/no regrets strategy as it has potential to mitigate the adverse effect of climate change. It may thus possibly lessen the emphasis of genetically modified crops for Sodic Haplusterts of the SAT, and is ready for its wide adaptation through national and international initiatives.

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(Received July, 2012; Accepted October, 2012)

Clay Research, Vol. 31, No. 2, pp. 109-119 (2012)

Removal of a Cationic Dye from Aqueous Solution using Bentonite

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Abstract: *Pollution of water by use of dyes is a widespread phenomenon and malachite green has been most often associated with aquatic pollution. This paper reports the ability of bentonite to remove malachite green from aqueous solutions by varying the amount of adsorbent, pH, temperature, and contact time and dye concentration in batch adsorption studies. It was found that adsorption increased with increasing pH up to 11 and temperature up to 50 °C and equilibrium was achieved within 30 minutes of contact time between bentonite and malachite green. More than 99% of the dye could be removed by using only 3 g bentonite per litre of dye. Adsorption of malachite green onto bentonite could be described by the first order kinetic model and could be well described by the Freundlich adsorption isotherm. Using the Freundlich isotherm, the absorption capacity of bentonite was found to be 17.56* $ug^{1-1/n}\,ml^{1/n}\,g^{-1}$ *at 30°C and hence is a promising low cost material for removal of dyes from waste water.*

Key words: Malachite green, bentonite, kinetics, adsorption isotherm, pollution

Introduction

Water is a scarce commodity and per capita water availability is set to decrease from 2150 to 1860 cubic meters by 2030 (IWMI, 2009). Water pollution is a major concern of the world today and governments of numerous countries are trying to find solutions to reduce this problem. A large number of Indian rivers are severely polluted as a result of discharge of sewage (CPCB, 2008) into them. The effluents from dye manufacturing and consuming industries are highly coloured coupled with high chemical and biochemical oxygen demands and suspended solids. Discharge of such effluents imparts colour to receiving streams which not only affects its aesthetic value but also inhibit the penetration of sunlight, with a consequent reduction in photosynthetic activity. This leads to disturbance in the ecological equilibrium.

Dyes are synthetic aromatic organic compounds, which are normally used for coloration of various substances and are widely used in many industries such as textile, carpet, paper, plastic, leather tanning, pharmaceutical and cosmetic

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***Corresponding author:** e-mail: amlankumar@yahoo.com industries (Gercel *et al*., 2008; Karaca *et al*., 2008). Today, dye pollutants from various industries are important sources of environmental contamination. Dyes are generally stable to light, oxidizing agents and heat, and their presence in wastewaters offers considerable resistance to their biodegradation, thus upsetting aquatic life (Robinson *et al.,* 2001; Aksu 2005). Some dyes have mutagenic, carcinogenic and teratogenic effects either when inhaled or when in contact with the skin and thus affect human health. Of current world production of dyestuffs (≈10 million kg/year) between 1 and 2 million kg of active dye enter the biosphere, either dissolved or suspended in water, every year (Allen *et al*., 2003). These dyestuff pollute water bodies and make it unfit for aquatic life and cause human health hazard.

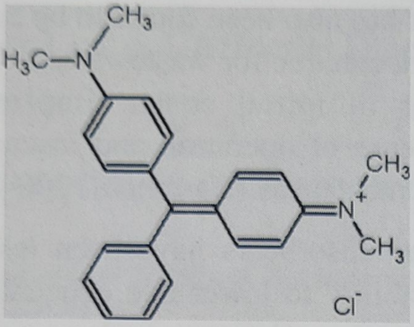
Although dyes are recognized easily even at low concentrations but removal and treatment of dyes from wastewater presents a very special challenge because such wastewaters cannot be treated by conventional treatment methods. Dyes exhibit considerable structural diversity and most of them are known to be non-biodegradable making it difficult to treat them by a single process (Southern, 1995). Since dyes are recalcitrant to the conventional aerobic biological treatment, eco-friendly and economical physical and chemical treatment processes need to be explored. Adsorption process is an efficient and economic process to remove dyes, pigments and other colorants (Wang *et al*., 2003). It has also been found to be superior to other technique for wastewater treatment in terms of initial costs, simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al*, 2004b).

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon, peat, chitin, and others (Tahir and Rauf, 2006). Activated carbon is the most popular adsorbent and has been used with great success (Erdem *et.al,* 2004). However, due to the difficulty and expense involved in their regeneration, clays are considered as alternative low cost absorbent. Since clays are present as natural deposits and are abundantly available, they can be easily used and regenerated and have been proposed as an inexpensive removal technique (Orthman *et al.,* 2007). This study explores the feasibility of using commercially available bentonite as an eco friendly dye removal technology.

Materials and Methods

Materials used in the experiment

Malachite Green (MG) used in the experiment is a dye commonly used in the Eastern part of Uttar Pradesh in textile and carpet industries. The dye was obtained from Ranchem, a branch of Ranbaxy Industries Limited, with a product code M0050, Batch No. G022H04 and adsorption maxima between 616 and 620 nm. The dye is identified as Basic Green 4 and is commercially known as Malchite



Green and is identified by the IUPAC name as 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl aniline and empherical formula is $C_{23}H_{25}N_2Cl$; molecular weight 365 and structure depicted herein. We scanned the wavelength in the visible region and found that the adsorption maximum was 615. Henceforth all experiments using malachite green was measured at 615 nm.

Bentonite used in the experiment was obtained from Loba chemicals company and was used as received having Lot No. 524071201 with less than 0.1 g coarse particles remaining on 200 mesh sieve.

Bentonite is a 2:1 type hydrated aluminosilicate clay primarily composed of the smectite-class mineral montmorillonite. Its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica which, by isomorphous substitutions, require cations, denominated exchange cations, to compensate for the negative charges of their laminar edges. Bentonite has the capacity to exchange these cations with the ones present in aqueous solutions. Bentonite has many industrial applications as an adsorbent and has been used for heavy-metal-ion removal and wastewater treatment. The abundance and availability of this mineral coupled with its low cost, guarantee its continued utilization in the future as an adsorbent.

Determination of parameters affecting dye removal

The effect of absorbent concentration, initial dye concentration, time of contact, pH, and temperature was investigated. The optimum pH for greatest removal efficiency was obtained out by equilibrating 50 mg of bentonite for 120 minutes on a rotary shaker with a rotation speed of 120 rpm with 50 mg L^{-1} MG at different pH (2, 3, 4, 5, 6, 7, 8, 9, 10 and 11). The optimum contact time was obtained by equilibrating 50 mg of bentonite for 10, 20, 30, 40, 60, 120, 180, 240 and 360 minutes with 60, 80 and 100 mg L^{-1} MG and the effect of temperature on the adsorption process was investigated at 30, 40 and 50 °C. In order to determine the optimum adsorbent concentration, increasing amounts of bentonite (25, 50, 100, 200, 300, 400, 500 and 800 mg) was equilibrated for 120 minutes on a rotary shaker with a rotation speed of 120 rpm with 50 mg L^{-1} MG . The influence of dye concentration on removal efficiency was investigated with 50 and 300 mg of bentonite, shaken at 30°C for 90 minutes at 120 rpm with 100 ml of MG varying in strengths from 10 to 100 and 25 to 500 mg l^{-1} respectively. The amount of dye removed was calculated by subtracting the calculated concentrations from 50 mg

L^{-1}. The percentage of dye removed was found out from the ratio of the amount of dye removed and the amount of dye added, multiplied by 100 and reported as %.

Results and Discussion

Influence of adsorbent doze on adsorption

It was found that the removal efficiency of dye increased with the increase in the amount of bentonite used (Fig. 1). The percentage of dye removal increased from 89.4 to 99.7% with increase of adsorbent dose from 0.25–4.0 g L^{-1}. Increase in surface area which also results in increase in the number of active adsorption sites, resulting from the increase in adsorbent mass is probably the reason behind this observation. Saha *et al.* (2010) also reported an increase in adsorption with the increase in adsorbate concentration using a clayey soil. Naseem and Tahir (2001) studied the effect of lead adsorption on bentonite. They found that the percentage of dye adsorption as well as the distribution coefficient increased with increasing amount of adsorbent up to 500 mg. The percentage dye adsoption remained constant but the distribution coefficient decreased drastically thereafter. The percentage removal of dye increased with increase of bentonite dose, but not linearly ,the adsorption capacity for MG decreased with the increasing amount of adsorbent suggestive of a decrease in total and effective adsorption surface area available to dye molecules for adsorption sites. With increasing adsorbent mass, the amount of dye adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in equilibrium value with increasing adsorbent mass concentration. The maximum dye removal (99.8%) was observed at 8 g L^{-1}. However, this value was not very much different form the maximum removal obtained at 99.2% with an adsorbent doze of 3 g L^{-1} and hence

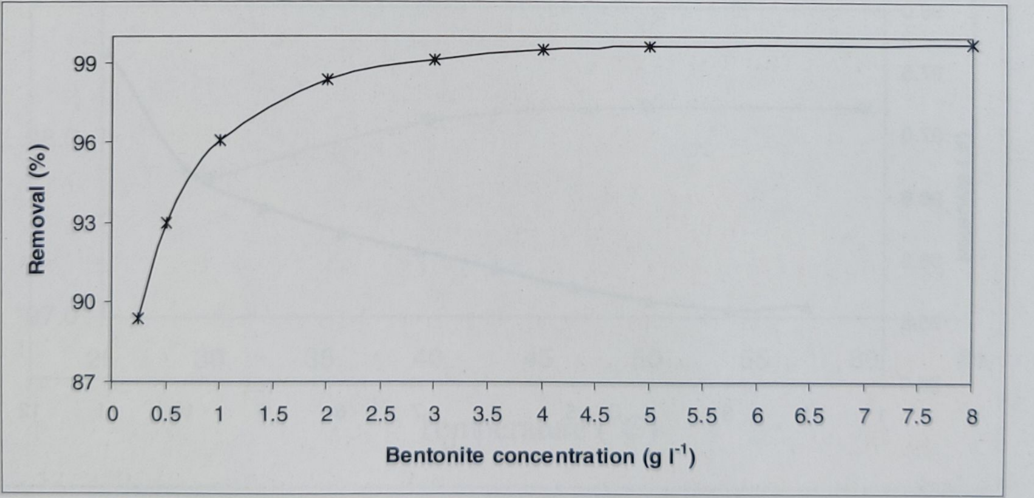


Fig. 1. *Influence of bentonite concentration on removal of malachite green from solution.*

was considered to be optimal for removal of malachite green dye. Naseem and Tahir (2001) however reported the optimum bentonite concentration for lead removal to be 0.5 g and Saha *et al*., (2010) observed the maximum removal of dye using clayey soil with adsorbent doze of 3 g L^{-1}.

Influence of pH on adsorption

pH is an important variable that controls the adsorption at the clay–water interface. In this study, changes in pH of MG solution had little influence of adsorption capacity of bentonite in the acidic range of pH (Fig. 2). At pH 2 the dye removal was 95.6% and it was 95.9% at pH 6. In bentonite-aqueous solution systems, the potential of the surface is determined by the activity of H^+ ions (or pH), which react with the bentonite surface. For the bentonite mineral, the potential determining ions are H^+ and OH^- and complex ions formed by bonding with H+ and OH^-. The broken Si–O bonds and Al–OH bonds along the surfaces of the clay crystals result in hydrolysis (Tahir and Rauf, 2006).

At low pH the reaction was as follows

$$>MeOH + H^+ \rightarrow >MeOH_2^+$$

The positive charge developed at the bentonite surface restrict the approach of positively charged dye cations to the surface of the adsorbent resulting in lower adsorption of dye in acidic solution. As the pH of the system was increased, the adsorption increased from 96.03% at pH 7 to 97.6% at pH 11. This increase in adsorption is because of de-protonation on the adsorbent surface as a result of increase in pH that results in increase in the negative charge density on the adsorbent surface and facilitates the bonding of the dye with bentonite. The reaction may be represented as follows:

$$>MeOH + OH^- \rightarrow >MeO^- + H_2O$$

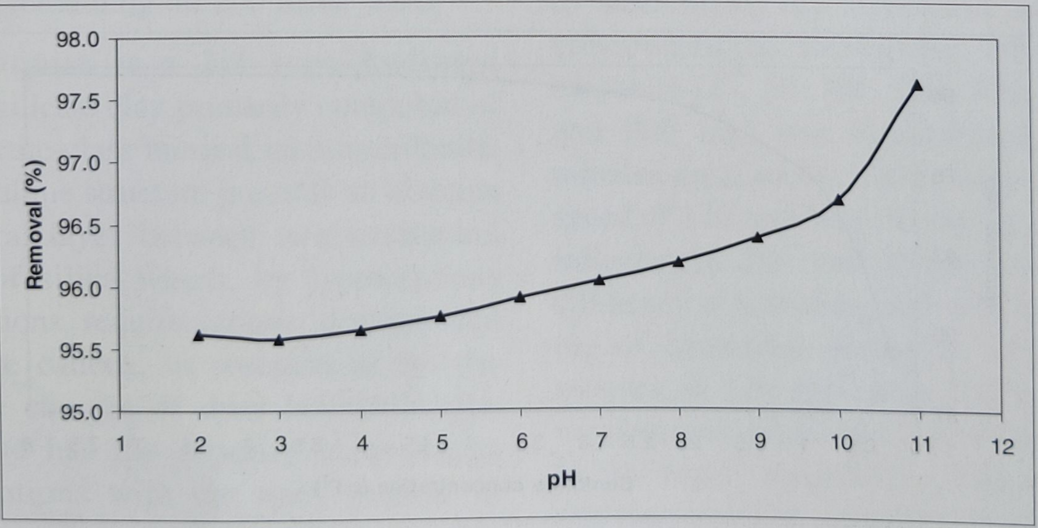


Fig. 2. *Influence of pH on the removal (%) of dye from aqueous phase.*

$$>MeO^- + MGCl \rightarrow >MeO^- MG^+ + Cl^-$$

where, Me is Al or Si and MG is the dye molecule.

But there are contradictory results about the effect of pH on the organic cation adsorption in the literature. For example, Tahir and Rauf (2006) found that dye adsorption capacity of bentonite increases with increasing pH. On the other hand, Bilgic (2005) have reported that the adsorption capacity of bentonite was essentially independent of pH in the range 2–11.5.

Influence of temperature on adsorption

Adsorption experiment using bentonite was carried out between 30 and 50 °C using a MG concentration of 50 mg L^{-1} and equilibration time of 90 minutes. The results indicate (Fig. 3) that MG uptake increased slightly with increase in temperature between 30 and 50°C. The observed increase in the adsorption capacity with increase of temperature from 30 to 50°C indicates that high temperature may favour the removal of MG and that the adsorption process is endothermic in nature. Saha *et al*. (2010) and Chowdhury and Saha (2010) however reported that adsorption process is exothermic and at high temperature the thickness of the boundary layer decreases due to increased tendency of the dye molecules to escape from the adsorbent surface to the solution phase, which results in a decrease in the adsorption capacity as temperature increased.

Influence of contact time on adsorption

The time dependent dye adsorption behaviour was measured by varying the equilibrium time between three concentration of malachite green viz., 60, 80 and 100 mg L^{-1} and 50 mg adsorbent in

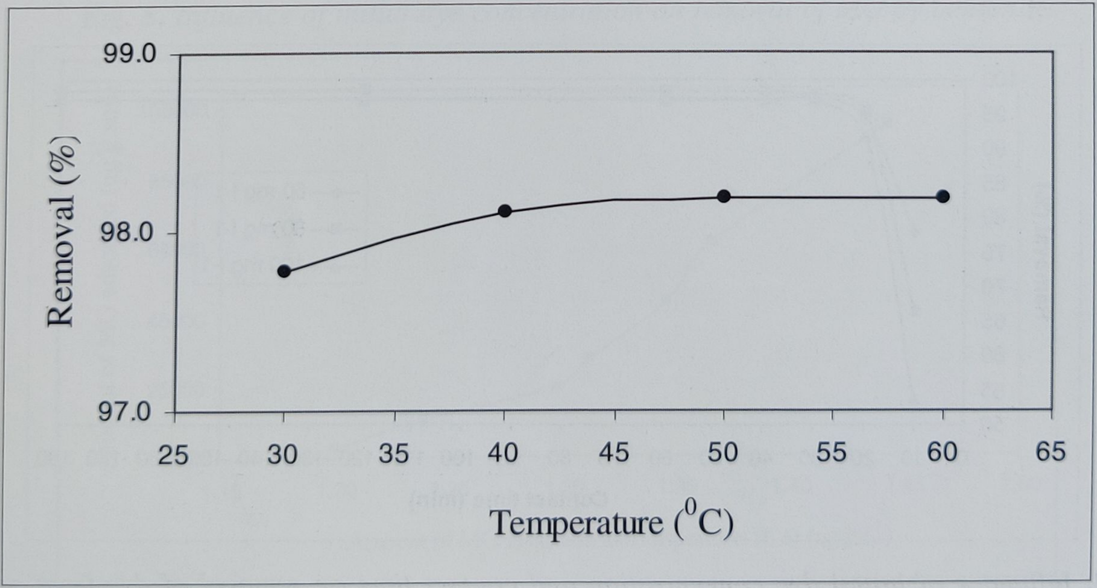


Fig. 3. *Influence of temperature on the removal of dye from aqueous solution.*

the range of 10 to 360 min at 30°C temperature. The equilibrium between the dye and bentonite was found to increase between 10 and 20 minutes (Fig. 4). After 30 minutes, no further increase in % of dye removal was observed. Adsorption was found to be more at lower initial concentration than at higher initial concentration at small equilibrations times (between 10 and 20 minutes) but these differences levelled off as the equilibration times increased and equilibrium was attained. Tahir and Rauf (2006) reported a 10 minute equilibration time for adsorption of malachite green oxalate on bentonite and Naseem and Tahir (2001) reported the equilibrium between lead and bentonite was attained within 10 minutes. However, Bulut *et al.* (2008) reported a 60 minute equilibration time for adsorption of malachite green onto bentonite. Three consecutive steps are involved in the removal of dye from water on bentonite (Tahir and Rauf, 2006). At first, the adsorbate species migrate from the bulk liquid phase to the outer surface of adsorbent particles (film diffusion). Secondly, the dye species move within the micro and macro-pores of adsorbent particles (pore diffusion). Thirdly, the reaction of adsorbate–adsorbent species takes place on the surface.

Influence of dye concentration on adsorption

The effect of initial dye concentration on the adsorption of MG on bentonite was studied at 3.0 g L^{-1} and the initial MG concentration of 25 to 500 mg L^{-1} (Fig. 5). It was found that as the initial dye concentration increased from 25 to 500 mg L^{-1}, the absolute amount of dye removed increased, but the equilibrium concentration did not change much and was practically

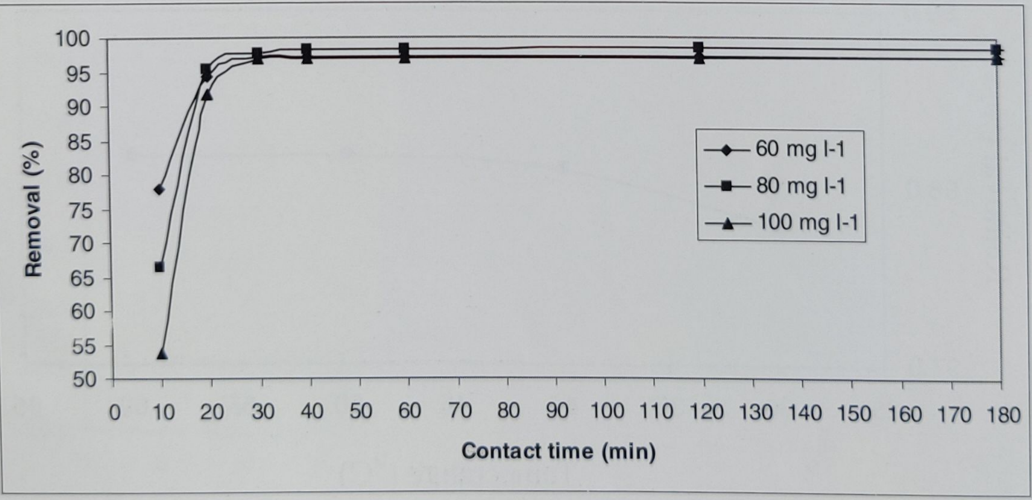


Fig. 4. *Influence of initial dye concentration and contact time on removal of dye from aqueous solution by bentonite.*

constant. This is probably because of the fact that, increasing the initial dye concentration results in an increase in the adsorption capacity because it provides a driving force to overcome all mass transfer resistances of dyes between the aqueous and solid phase (Baek *et al.*, 2010). The amount of dye removed increased from 95.2 to 99.4% as the initial dye concentration increased from 25 to 500 mg L^{-1}. It is suspected that sorbent saturation has just been achieved and further increase in MG concentration would have resulted in decrease in amount of dye removed.

Adsorption and Kinetic studies

Plotting the solid phase concentration against liquid phase concentration, graphically it is possible to represent the equilibrium adsorption isotherm (Fig. 6). Thus, the isotherm yields certain constants whose values express the affinity and

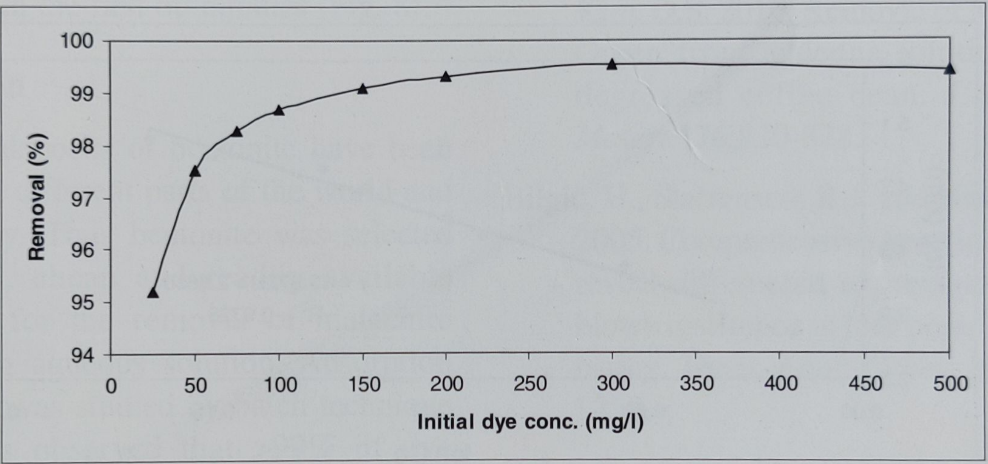


Fig. 5. *Influence of initial dye concentration on removal of MG by bentonite.*

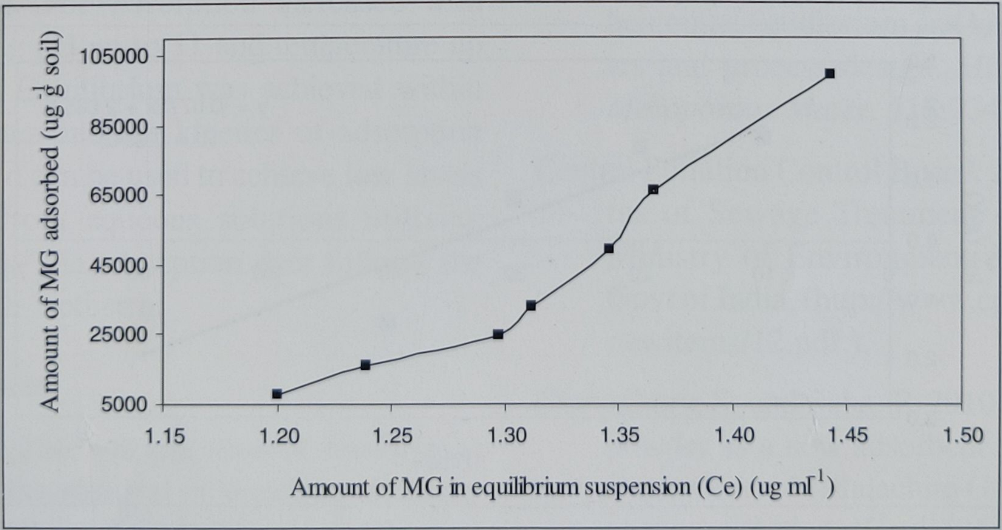


Fig. 6. *Adsorption isotherm of malachite green on bentonite.*

surface properties of the adsorbent. Our adsorption data could be described by the linearised form of Freundlich adsorption equation viz., $\log(x/m) = \log K + 1/n \log C_e$, where K and 1/n are constants associated with the affinity of bentonite for malachite green and the degree of curvature of the isotherm respectively. The correlation coefficient of the data was greater than 0.97, suggesting a good fit of the experimental data. The value of K and n for adsorption of malachite green on bentonite was estimated by linear regression of the logarithmically transformed data (Fig. 7) and were 17.56 $ug^{1-1/n}\ ml^{1/n}\ g^{-1}$ and 0.072$g\ l^{-1}$ respectively. The magnitude of K expresses the adsorption capacity whereas 1/n values provide an idea of the intensity of adsorption. The value of K computed here is close to the value reported by Tahir and Rauf (2006) for bentonite.

The chemical kinetic describes reaction

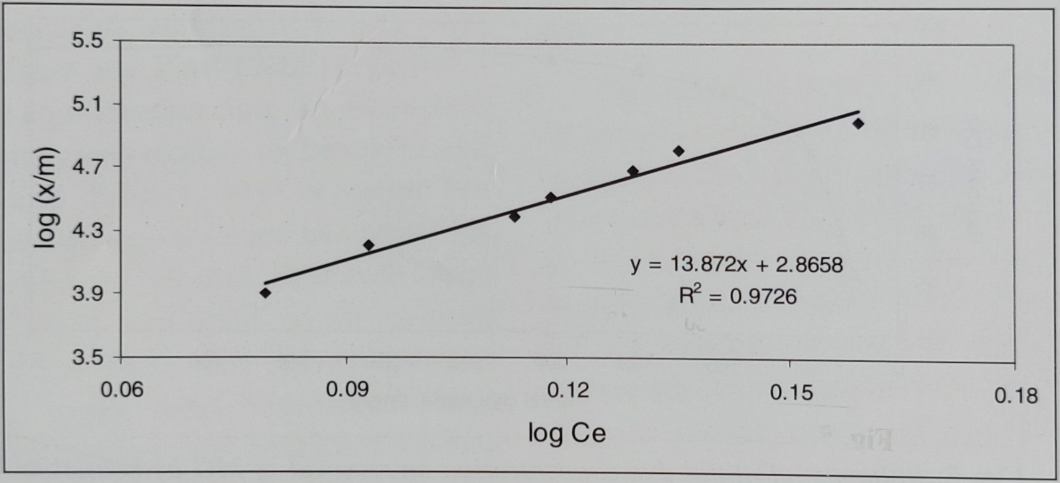


Fig. 7. *Freundlich adsorption isotherm of malachite green on bentonite.*

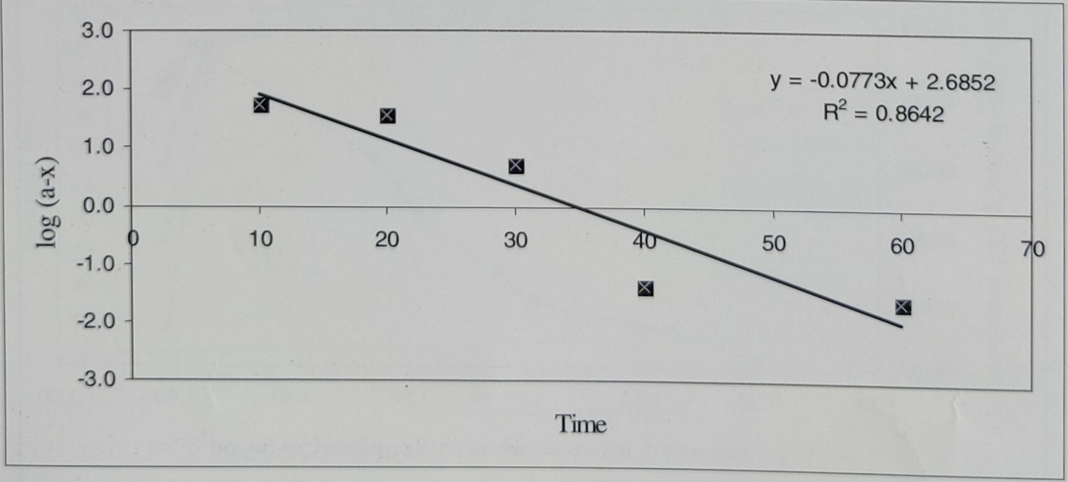


Fig. 8. *Kinetics of malachite green adsorption onto bentonite at 100 mg l^{-1} dye concentration.*

pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. In recent years, adsorption mechanisms involving kinetics-based models have been reported. We investigated the first order kinetic model to investigate the mechanism of adsorption and found that the plot of log (a-x) verses time, where *a*, is the initial concentration and *x*, the equilibrium concentration at time *t*, to be linear within the first 60 minutes (Fig. 8).

Conclusion

Large deposits of bentonite have been reported in different parts of the world and our country. Thus bentonite was selected as a local, cheap and readily available adsorbent for the removal of malachite green from aqueous solution. Adsorption of the dye was studied by batch technique and it was observed that >99% of dye removal was achieved by using 0.3 g of bentonite. The adsorption increased with increasing pH up to 11 and temperature up to 50°C. Equilibrium was achieved within 30 minutes and the kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing bentonite. The adsorption data follows the Freundich isotherm.

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(Received January, 2012; Accepted October, 2012)

ACKNOWLEDGEMENT

CMSI acknowledges the revising/editing of the following persons:

1. Dr. D.K. Pal
2. T.K. Bhattacharyya
3. K.M. Manjaiah

INSTRUCTIONS FOR CONTRIBUTORS

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Clay Research

Vol. 31 December 2012 No. 2

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Printed at : Cambridge Printing Works, New Delhi-1100028. (Mobile : 9811860113)